THE EFFECT OF WATER QUALITY AND CHEMICAL COMPOSITION ON THE CORROSION OF MILD STEEL PIPELINES

BY

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EXECUTIVE SUMMARY

Corrosive potable water can cause financial losses in water reticulation and distribution systems as well as plumbing in buildings. This may add up to millions of Rands per annum for maintenance. If important factors that may influence the corrosiveness of water can be determined in advance, purification processes could be adapted to prevent or reduce corrosion.

In the first instance the aim and objective of this investigation was to increase the knowledge of chemical stabilisation of potable water. All indices that describe the chemical saturation state, stability, or corrosiveness of potable water show some shortcomings. Although the Langelier saturation index is applied generally to determine if a water is corrosive or not, it's predictions are seldom correct and it seldom correlates with predictions of other indices. The chemical conditions in water for which each index is applicable are not clear and a need exists to establish guidelines for the use of different indices in water. The second aim was to determine the extend to which water must be treated to ensure that the water quality will remain constant between the purification plant and the consumer. It will be ideal if the chemical changes that may occur, can be predicted beforehand so that preventative treatment can be applied. Corrective post treatment of water in a distribution system to ensure chemical stability has not received much attention up to now, probably because of practicalities, a lack of knowledge with regard to the chemical mechanisms involved and uncertainty of what the effect of secondary treatment will have on the water quality. It is, therefore, important for this aspect to be investigated so that the local distributor can be informed how to treat the water if necessary. The knowledge obtained, could lead to economic benefits, because it can help to extend the life of pipe systems and thereby effect considerable savings. Other benefits that evolved from this investigation is the characterisation of a stable, non-corrosive water, identification of the most applicable index for a specific set of water conditions, determination of possible relationships between chemical composition of potable water and corrosion rates of mild steel and improvement of the water quality reaching the consumer.

The investigation incorporated laboratory scale tests, as well as scaled down pilot plant investigations using through flow pipe systems. The chemical composition of Sterkfontein Dam water that was used as a standard, was adjusted for specific test runs for most of the investigations. Vaal Dam water was used in some cases. Water produced by Rand Water was used during the investigation on corrosion monitoring and control in distribution systems. Corrosion rate measurements were conducted using mild steel coupons, the Rohrback Corrater, Model 1120, and two types of electrode systems for the electrochemical interface technique (Tafel extrapolation).

During the laboratory investigation, the effect on corrosion of different chemical species and compounds such as; chloride, sulphate, chlorine, nitrate, alkalinity, oxygen and organic flocculants, were determined. The effect of temperature, pH and the Calcium Carbonate Precipitation Potential (CCPP) were also studied. Actual corrosion rates measured on coupons were compared to the values predicted by the different indices. The latter determinations were based on chemical and physical properties. Indices evaluated were the Langelier Saturation Index, Ryznar Stability Index, Driving Force Index, Aggressive Index, Riddick Corrosion Index, Larson Index and Casil Index as well as the Feigenbaum GalYahalom combination.

Corrosion rates and variations in chemical and physical properties were monitored in continuous flow systems. The effect of corrosion inhibitors such as silicate and monochloramine as well as the effect of linear flow rate were examined.

The following conclusions, based on the results can be made:

1. There is a direct relationship between the corrosion rate of mild steel and the conductivity and hence the total dissolved solids content of water which is a function of the type and concentration of different chemicals present. Temperature also plays an important role. Three equations were developed by Rand Water with which the corrosiveness of water towards mild steel, based on the relationships above, can be predicted in microns per year. These equations are called the Conductivity based Corrosion Equations (C-Rate) and the calculated corrosion rate is given by CRm. The first equation C-Rate(Prog), gives the corrosion rate based on a computer program developed by Rand Water and incorporates a variety of chemical and physical factors measured in water.

   $\mathrm{CRm} = [4{,}09\ \mathrm{Cl}^- + 4{,}0\ \mathrm{SO}_4^{2-} + 2{,}79\ \mathrm{Cl}_2 + 9{,}78\ \mathrm{NO}_3\text{-N} + 3{,}12\ \{T_{alk} - \mathrm{CCPP}/F_1\} + 9{,}98\ pH - 118]\ F_1F_2$,

   while the second equation, C-Rate(Cond)

   $\mathrm{CRm} = 12{,}9\ \mathrm{mS/m} - 4{,}74$,

   and third, C-Rate (TDS),

   $\mathrm{CRm} = 1{,}9\ \mathrm{TDS} - 3{,}84$,

   can be applied if either the conductivity (Cond) or the total dissolved solids (TDS) content of the water is known. Important observations were firstly the fact that increasing alkalinity present as bicarbonate (HCO_3^-) led to a proportional increase in initial corrosion rates caused by a proportional increase in conductivity and secondly that increasing chloride and sulphate concentrations also led to a proportional increase in corrosion rates of mild steel caused by proportional increases in conductivity.

2. Based on the effect of mainly alkalinity on the corrosion of mild steel, it was possible to characterise the chemical composition range of a stable and relatively non corrosive water. To compile the data, corrosion rates were measured over a long period in water with different chemical composition. Actual corrosion rates were measured on metal coupons, the corrater and Tafel extrapolations. Expected corrosion rates for the same water samples, based on the chemical analyses of the samples were calculated using the equations developed by Rand Water, and standard corrosion indices. These values were calculated for different CCPP values and alkalinity concentrations and the chemical composition of water which had corrosive or protective properties according to the calculated or measured methods were defined. The range of the chemical composition of water, with good protective properties was then fixed. The validity of

the chosen chemical composition was tested by comparing the actual measured corrosion rates with calculated indices values. In most cases the calculated index values agreed with the measured corrosion rates. The analysis of water which has the potential of being neither corrosive or aggressive in contact with mild steel is given in the table below:

ANALYSIS	RANGE
Conductivity mS/m	14,5 - 17,0
pH	8,3 - 8,6
TDS mg/ℓ	97,4 - 116
Alkalinity as mg/ℓ $CaCO_3$	71 - 89
Hardness as mg/ℓ $CaCO_3$	69 - 73
Calcium mg/ℓ	19 - 25
Magnesium mg/ℓ	2,6 - 3,4
Sodium mg/ℓ	3,9 - 10,0
Iron mg/ℓ	0,05 - 0,61
Activated SiO_2 mg/ℓ	4,0 - 9,6
Total SiO_2	9,0 - 10,0
Ammonia mg/ℓ	<0,05
Nitrite-N mg/ℓ	<0,30
Nitrate- N mg/ℓ	0,11 - 0,69
Sulphate mg/ℓ	<5
Chloride mg/ℓ	<5

3. With regards to the value of the different indices to predict the corrosiveness of water, it must be concluded that the results obtained are only as good as the terms and factors incorporated in their equations. For example, the Langelier, Ryznar, Driving Force and Aggressive Indices only predict the possibility for calcium carbonate to precipitate or dissolve. The assumption is then, if precipitation takes place, protection against corrosion will occur. The CCPP is the only "index" with which the precise amount of calcium carbonate that may precipitate or dissolve, as well as the equilibrium alkalinity and pH, can be determined. In this regard it could be most useful as an operational parameter used in the water purification process.

Other chemical factors which could effect the corrosiveness of water are also utilised in equations of all the other indices. However, to obtain a full picture of the nature of water it is proposed that a combination of indices should be used in each case. For this reason computer programs have been developed in this project to calculate the values for the different indices, CCPP, equilibrium of alkalinity and pH as well as the corrosion rate equations developed by Rand Water. A laboratory type method that can be used, if the computer programs are not available, was developed to determine the CCPP, equilibrium alkalinity, pH and the Langelier Saturation Index. These methods are suitable to determine the chemical stability of water in distribution systems.

4. The inhibiting effect of some chemical determinants, eg. activated and non-activated silicate, and monochloramine were investigated. The use of non-activated silicate resulted in a decrease in corrosion rate for silicate content up to 10 mg/ℓ as SiO_2 and an increase in corrosion rate for silica higher than 10 mg/ℓ. Activated silicate led to an increase in the corrosion rate. At a concentration of 1 mg/ℓ monochloramine may act as a corrosion inhibitor.

   It is proposed that a more extensive investigation be done to determine the inhibiting effects of the determinants discussed above.

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MEANING OF SYMBOLS AND EQUATIONS

A = Surface area of working electrode in cm^2.
A^1 = Function of water temperature in the equation of pHs.
A_1 = Surface area of coupons to the nearest 0,01 cm^2.
A_2 = Constant: 0,0035 used in Y index equation.
A_3 = Temperature dependent constant; $1{,}825 \times 10^6 (78{,}3xT)^{-1{,}5}$
AI = Aggressive Index

B = Constant; 0,34 used in Y index equation.
B^1 = Function of ionic strength in the equation of pHs.

C = Concentration in corrosion rate equations in mg/l.
C_1 = Constant; 19,0 used in Y index equation.
c = Carbonate concentration (in mg/ℓ $CaCO_3$).
Ca_{hard} = Calcium hardness.
Calo.RE = Electrode configuration with calomel reference electrode.
C-Rate(Prog) = Conductivity based Corrosion Equation - chemical compound
C-Rate(Cond) = Conductivity based Corrosion Equation - conductivity
C-Rate(TDS) = Conductivity based Corrosion Equation - total dissolved solids
CCPP = Calcium carbonate precipitation potential.
CCPP-SS = Calcium carbonate saturation state.
CI = Casil Index.
Con = Conductivity in mS/m.
CR = Corrosion rate in micron per year (μm/y).
CRcal = Calculated corrosion rates in μm/y.
CRm = Measured corrosion rated in μm/y.
CR_T = Total corrosion rate.
C_T = Total carbonic concentration.

d = Density of mild steel in g/cm^3.
DFI = Driving Force Index.

E = Equivalent weight of mild steel in gram; g.
e = Chloride concentration (in mg/ℓ Cl^-).
ECI = Electrochemical interface.
E_{corr} = Corrosion potential.
E_{pit} = Pitting potential.
E_{prot} = Protection potential.
E_{cr} = Critical potential.

log fi = $-A_3Zi^2 [\mu^{1/2}/(1 + \mu^{½}) - 0{,}3\mu]$.
fi = Activity coefficient for species i, written as Fm and Fd for mono and divalent ions respectively.
F = Faraday's constant; ≈ 95000 coulomb.

F_1 = Factor for oxygen concentration.
F_2 = Factor for temperature in degrees Celsius.

H = Factor; $(Ca^{2+})(HCO_3^-)^2/(CO_2)$ in Y index.
H_1 = Hardness in mg/l $CaCO_3$
h = Bicarbonate (HCO_3^-) as mg/l $CaCO_3$.
H^1_s = Molal concentration of H^+ when it is at pHs. (Stability pH)

I = Current flowing through metal.
I_{corr} = Current at corrosion potential E_{corr}.
Ion strn. = Ionic strength (μ).

JTG = Joint Task Group on Calcium Carbonate Saturation, JAWWA.

k = Rate constant for conversion of Fe^{2+} to Fe^{3+}.
k_1 = Constant in corrosion rate equation for coupons with value of $8,76x10^7$ if corrosion rate is measured in microns per year.

ℓ = Litre.
LI = Larson Index.
LSI = Langelier Saturation Index.

mpy = mils per year (thousands of an inch per year).
Mild S.RE = Electrode configuration with mild steel reducing bush as reference electrode.
M = Mass of metal dissolved.

n = Nitrate concentration (in mg/ℓ NO_3^-).
NTU = Nephelometric units for measuring turbidity.
K_1 = First ionic product constant for carbonic acid with all species expressed as activities, ( ).
K_2 = Second ionic product constant for carbonic acid with all species expressed as activities, ( ).
K_w = Ionic product constant for water with species expressed as activities, ( ).
K_{sol} = Solubility ionic product constant for $CaCO_3$ with species expressed as activities, ( ).
K_1^1 = First apparent equilibrium constant for carbonic acid with species expressed as molar concentrations, mol/l, [ ].
K_2^1 = Second apparent equilibrium constant for carbonic acid with species expressed as molar concentrations, mol/l, [ ].
K_w^1 = Apparent equilibrium constant for water with specie concentration expressed as molar concentrations, mol/l, [ ].
K_{sol}^1 = Apparent solubility equilibrium product for $CaCO_3$ with species concentration expressed as molar concentrations, mol/l, [ ].

O = Opposite

pe = Redox function (redox potential as the negative logarithm of the electron activity)

pK_1 = Negative logarithm of first ionic product constant for carbonic acid with temperature dependant equations; 17052/T + 215,21 log T - 0,12675T -546,56.
pK_2 = Negative logarithm of second ionic product constant for carbonic acid with temperature dependant equation; 2902,39/T + 0,02379T - 6,498.
pK_w = Negative logarithm of ionic product constant for water with temperature dependant equation; 4787,3T + 7,1321 log T + 0,01037T - 22,801.
pK_{sol} = Negative logarithm of the solubility ionic product constant with temperature dependant equation; 8,03 + 0,01183T.
pK_2^1 = Negative logarithm of the second apparent equilibrium constant for carbonic acid.
pK^1_s = Negative logarithm of apparent solubility equilibrium product for $CaCO_3$.
pCa = Negative logarithm of the molal concentration of calcium.
pAlk = Negative logarithm of the equilibrium concentration of titratable acid.
pO_2 = Partial pressure of dissolved oxygen in atmosphere.
pH_s = Equilibrium pH calculated according to Langelier.
pH_{eq} = Equilibrium pH calculated according to the JTG method.
$pAlk_{eq}$ = Equilibrium alkalinity calculated according to the JTG method.
PVC.Carb.RE Electrode configuration with carbon reference and counter electrodes with PVC reducing bush.

r = Regression coefficient.
Redox function Redox potential as negative Logarithm of the electron activity (pe)
RCI = Riddick Corrosion Index.
RSI = Ryznar Stability Index.
Sd = Total dissolved solids (TDS) in mg/l.
S = Similar.
S' = Partly similar.
s = Sulphate (SO_4^{2-}).

T = Kelvin (273°C + t).
t = Temperature in °C.
T_1 = Exposure time in hours to the nearest 0,01 hour.
Talk = Total alkalinity in mg/l $CaCO_3$.
Thard = Total hardness (mg/ℓ $CaCO_3$
Tacid = Total acidity.

w = Mass loss in g, to the nearest 1 mg.

X_1 = T_{alk} x 10^{-5} - ($[OH^-]/2$ - $(H^+)/2$).

Y = Feigenbaum, Gal-or, Yahalom combination Index.
Y_1 = $0,5 + K_2 fm/fd(H^+)$.
y = year

Zi = Charge on species i equal to one for mono and two for divalent ions.
Z_1 = fd $(H^+)/2$ k_2 fm + 1.

μ = Ionic strength with equation; 2,5 x 10^{-5} Sd.
μA = Microampêre

1 INTRODUCTION

1.1 EXTENT AND IMPORTANCE OF CORROSION

All potable waters reveal corrosive properties to a greater or lesser extent. Corrosiveness increases with long retention times in distribution systems where it can come into contact with clean metal surfaces. Although provision is made at water purification plants to produce chemical stable and non-corrosive water, it is not always successful. Even the dosage of chlorine, that is an essential step in the purification process, can increase the corrosiveness of potable water.

Corrosive water has aesthetic and economical consequences. Red water, for instance, caused by corrosion of mild steel distribution systems is unacceptable for local authorities and consumers. Direct financial damage can occur because of the loss of stained cloths and sanitary equipment like baths and wash-basins. Financial loss due to corrosion in distribution systems of local authorities and pipe systems in buildings may add up to millions of Rand per year because of high maintenance costs.

A change in the quality of raw water sources, as is experienced with the use of water from the Tugela-Vaal pump storage scheme and that will be experienced with the implementation of the Lesotho - Highland scheme can have a substantial influence on the quality of potable water that will be produced. The changes in chemical composition will have an effect on the corrosive properties of the water. If important factors, that may influence the corrosiveness of water, can be determined in advance, the purification process can be adapted to prevent or reduce corrosion.

1.2 AIMS AND OBJECTIVES OF THE PROJECT

1.2.1 Increase the knowledge of chemical stabilisation of potable water

All indices that describe the saturation state, stability or corrosiveness of potable water show some shortcomings. Although the Langelier saturation index is generally applied to determine if a water is corrosive or not, it's predictions are seldom correct and it seldom correlates with predictions of other indices. The water conditions for which each index is applicable are not clear and a need exists to determine guidelines for the use of different indices in water.

1.2.2 Quality of water reaching the end consumer

It is important to provide only water of the highest quality to the consumer. Changes occurring during the distribution of the water ought not to be detrimental to the consumer with regard to aesthetic, health and financial aspects. The aim must be to treat water in such a way that the quality will stay the same between the purification plant and the end consumer. It will also be ideal if the chemical changes that may occur, can be predicted beforehand so that preventative treatment can be applied.

The post treatment of water in a distribution system to ensure chemical stability has not received much attention up to now, probably because of the practical aspects involved, lack of knowledge with regard to the chemical mechanisms and uncertainty of what the effect of secondary treatment will have on the quality of the water. It is therefore important for this aspect to be investigated so that the local distributor receiving water from a bulk supplier can be informed how to treat the water if necessary.

1.2.3 Economic reasons

Application of the knowledge obtained could help to extend the life of pipe systems and thereby effect considerable savings.

1.3 BENEFITS THAT CAN EVOLVE FROM THIS INVESTIGATION

1.3.1 The characterization of a stable, non-corrosive water.

1.3.2 Identification of the most applicable index for a specific set of water conditions.

1.3.3 Determination of possible relationships between chemical composition of potable water and corrosion rates of mild steel.

1.3.4 Improvement of the water quality reaching the consumer

1.4 INVESTIGATION

Effects of different chemical species, e.g. chloride, sulphate, nitrate, alkalinity, hardness, chlorine, monochloramine, organic flocculants, silicates and oxygen as well as physical factors like temperature and hydraulic flow rate on corrosion were investigated.

Relationships between chemical and physical properties of water for different indices were determined.

Laboratory as well as a pilot plant investigations were done. In the latter instance through flow pipes were used to simulate a distribution pipe system and to determine the correlation with the laboratory investigation.

Corrosion rates were determined using mild steel coupons and electrochemically methods making use of a corrater and polarisation plots.

In the next chapter the instrumentation, materials and methods applied, will be discussed in more detail.

2. MATERIALS AND METHODS

Experimental procedures are discussed under the headings: instrumentation, preparation and handling of coupons and working electrodes, chemicals and stock solutions, samples and calculations.

2.1 INSTRUMENTATION

The following is a discussion of the instrumentation, electro chemical cells and test coupons used in this investigation.

2.1.1 Rohrback Corrater Model 1120

The Rohrback Corrater Model 1120 is battery (DC) operated and measures the corrosion rate directly in mils per year (mpy, thousands of an inch per year) via a probe consisting of two mild steel corrosion electrodes (two point electrode). The equation on which the corrosion measurements is based can be written as follows:-

$$\text{mpy} = \text{Meter reading} \times \frac{\text{Probe Multiplier}}{\text{calibration setting}} \times \text{Resistivity factor} \quad \text{.............(1)}$$

The corrater electrodes with RCS Alloy Code 8002 had surface areas of 5 cm^2, with multiplier factor of one. For all measurements a calibration setting of one had been used. Therefore the equation simplifies to

$$\text{mpy} = \text{Meter reading} \times \text{Resistivity factor}$$

The Resistivity factor is a factor by which the meter reading is multiplied to compensate for the resistivity of the sample. To obtain the resistivity factor the conductivity in μS/cm (micro Siemens per centrimeter) of the sample is measured and the corresponding resistivity (Ω cm) is read from a conversion graph provided by the suppliers. The obtained corrosion rates expressed as mpy are multiplied with 25,4 to convert it to microns per year (μm/y).

The operational range for the Corrater Model 1020 is for samples with conductivity greater than 10 μS/cm and corrosion measurements smaller than 1000 mpy (Rohrback instruments). All the water samples in this investigation had a conductivity greater than 10 μS/cm and therefore it was not necessary to use the conversion graph.

Corrater electrodes were corroded in deionised water for 24 hours (overnight) before they were used to measure corrosion rates.

2.1.2 Schlumberger Model 1286 Electrochemical Interface and Corrosoft Eric Program

The 1286 Electrochemical Interface (1286 ECI) may be used as a potentiostat or galvonostat. It controls and measures the DC characteristics of an electrochemical cell. In this investigation it was operated with a Corrosoft ERIC program supplied by Capcis in the United Kingdom. The 1285 ECI and ERIC program were used to obtain Tafel Plots, (figure 2.1) from which corrosion rates were calculated.

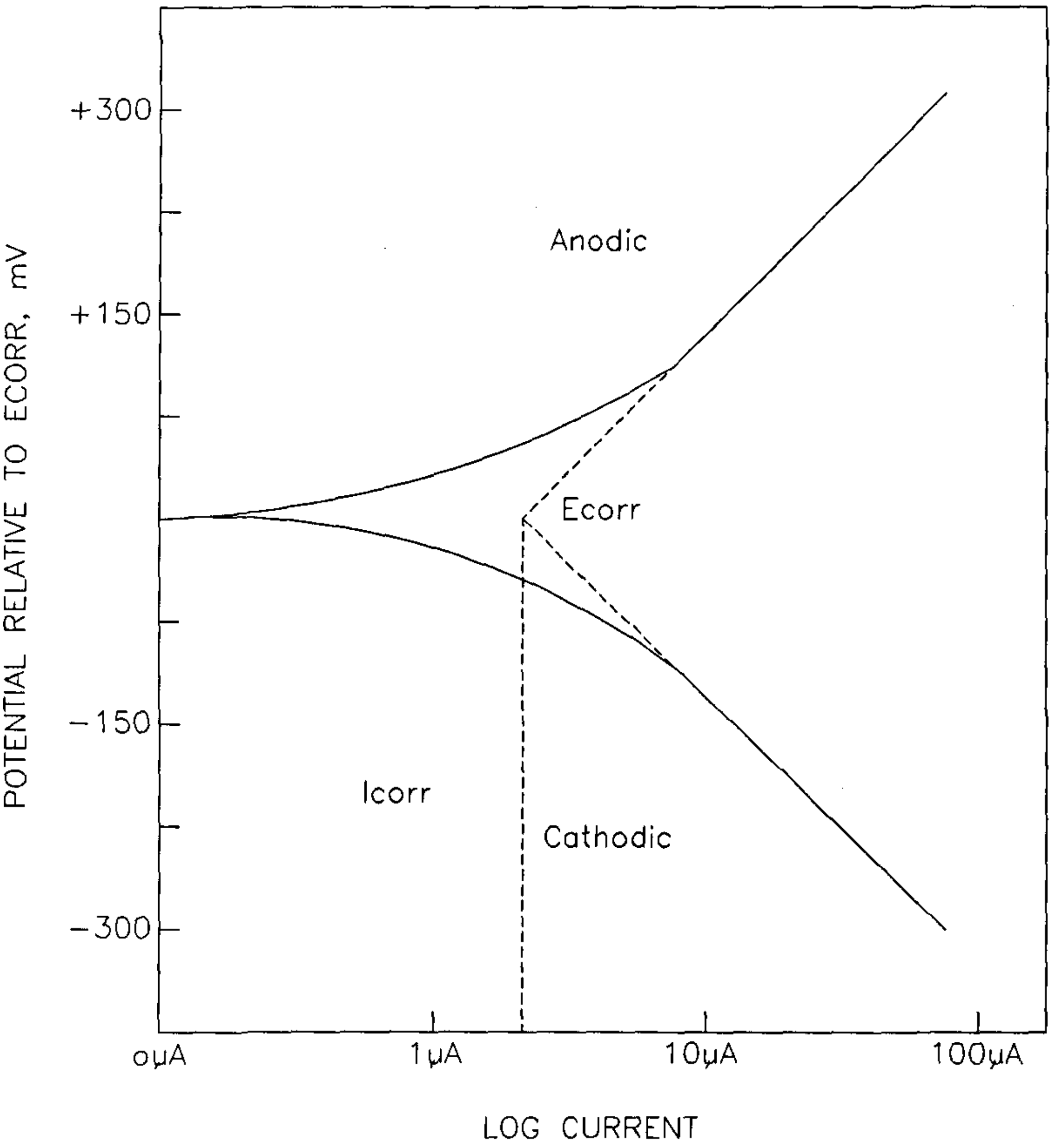


Figure 2.1 Tafel plot produced from experimental readings

CAD335D

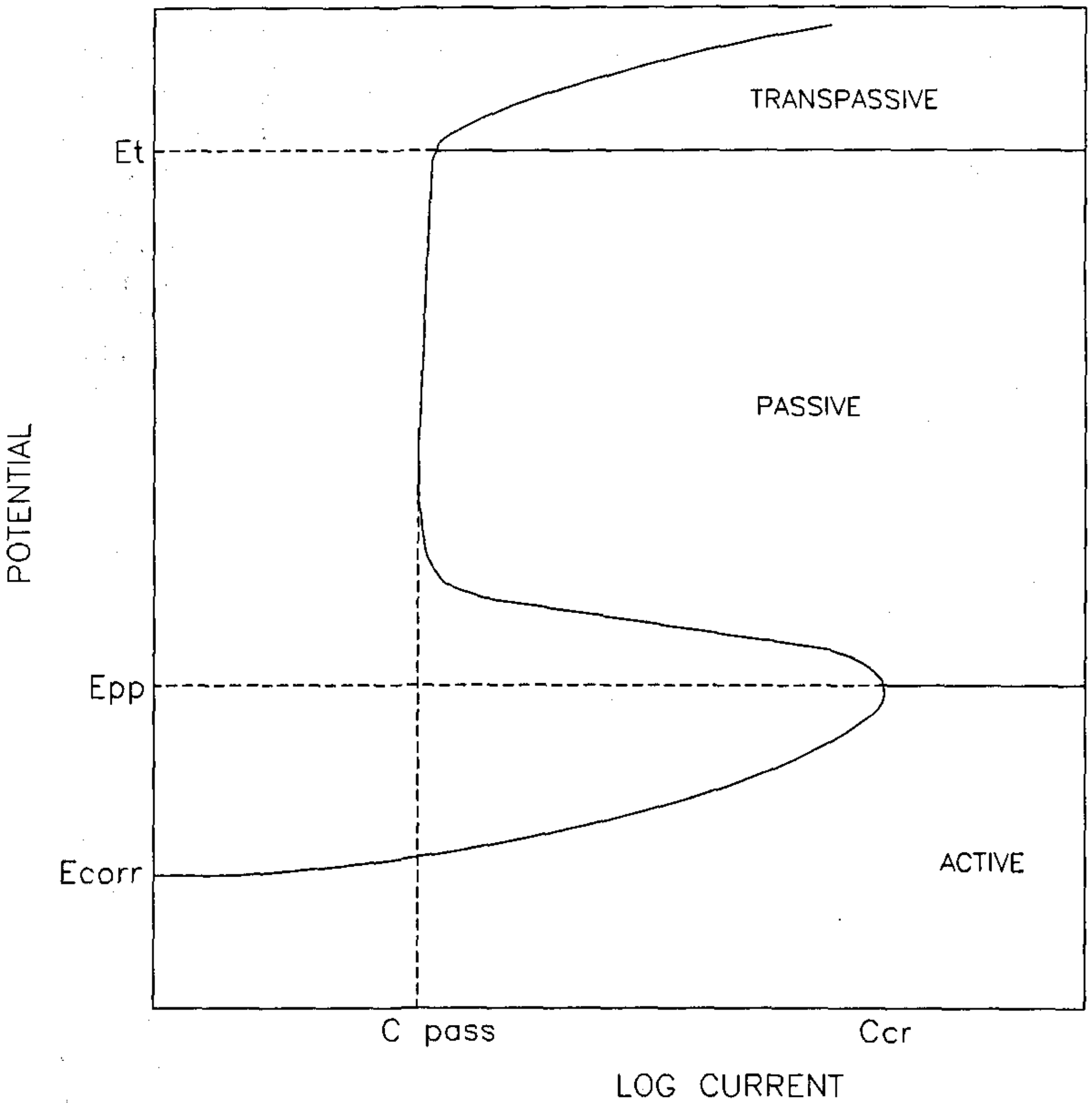


Figure 2.2 Potentiodynamic Plot

CAD335B

Tafel Plots are performed by polarizing the specimen (mild steel) about 500 mV cathodically (negative going potential) and anodically (positive going potential) from the corrosion potential, E_{corr}. E_{corr} is the potential of the specimen where the anodic and cathodic currents are equal in magnitude (see comments in paragraph 2.6.2). The 1286 ECI measures the corresponding current as it changes the potential on the metal surface, relative to a reference electrode, from 500 mV below E_{corr} to 500 mV above E_{corr}. The sweeping range can be adjusted as required. The potential and current coordinates are then displayed as a semi-log graph on the monitor, with the current on the log scale. The Tafel Plot (figure 2.1) is only that part of the total potentiodynamic polarization plot (figure 2.2) that includes the cathodic and active anodic current. For more details, see the discussion of the electrochemical techniques, paragraph 2.3. As oxygen affects the shape of the cathodic plot, Tafel Slopes were only determined from the anodic current Tafel Plot. The sweep and plot functions setting used with the Eric program are shown in Table 2.1a.

TABLE 2.1a: SWEEP AND PLOT FUNCTION SETTINGS

Sweep mode	Potentiostatic
Plot mode	log(i)/E
Sweep limit (1)	-500 mV
Sweep limit (2)	+500 mV
Number of sweep segments	one
Sweep rate	1V/min
Sweep time	1,25 min
Datum	E_{corr}
Emin	-500 mV
Emax	+500 mV
imin	1 μA
imax	1 A
Hold time at start of sweep	10 min
Electrode area	1,12 cm^2 for Calo.RE 0,665 cm^2 for PVC.Carb.RE 0,32 cm^2 for mild S.RE

TABLE 2.1b: BASELINE VALUES

(a) Laboratory investigation

Parameter	Value
Temperature °C	22 ± 0,5 °C
Stirrer speed	Medium
Dissolved oxygen - mg/ℓ	Saturation at 7,1 mg/ℓ
Stock solution	Sterkfontein Dam water

(b) Six and two pipe through flow systems

Parameter	Value
Temperature °C	22 - 24
Flow speed	5 m/min in six pipe system 9 m/min in two pipe system
Dissolved oxygen - mg/ℓ	Saturation at 7,1 mg/ℓ
Stock solution	Sterkfontein Dam water

2.1.3 Various Electrochemical cells

The electrochemical cell that was used in conjunction with the electrochemical interface consisted of a container for the water sample and three electrodes, the two main electrodes being the counter electrode and the working electrode. The third electrode is a calomel reference electrode against which the polarisation potential between the working electrode surface and the liquid phase is measured, normally via a Luggin capillary.

In this investigation three different probes were used within the electrochemical cells.

a) The **probe (Calo.RE)** (Figure 2.3) consisted of a calomel electrode without a Luggin capillary and a holder that contained a metal disc as a working electrode. The disc was 0,5 cm thick, with a surface area of 1,12 cm^2 held in position by a screw cap so that it made firm contact with a copper disc conductor. An 0-ring seal placed between the screw cap and working electrode isolated the copper disc from the water. Two carbon rods formed the counter electrodes. As a result of the conductivity of the water samples, poor Tafel Plots were obtained with a Luggin capillary. Therefore a calomel electrode without a Luggin capillary was used throughout the investigation.

b) The **second probe (Mild S.RE)** (Figure 2.4) consisted of a 25 - 19 mm galvanised reducing bush with a mild steel surface as a reference electrode. Embedded within an epoxy resin in the centre of this bush a carbon rod as a counter electrode, as well as a mild steel pipe section symmetrical around the carbon rod were mounted. The exposed ring section of mild steel with a contact surface area of 0,32 cm^2 acted as a working electrode with a contact surface area of 0,32 cm^2.

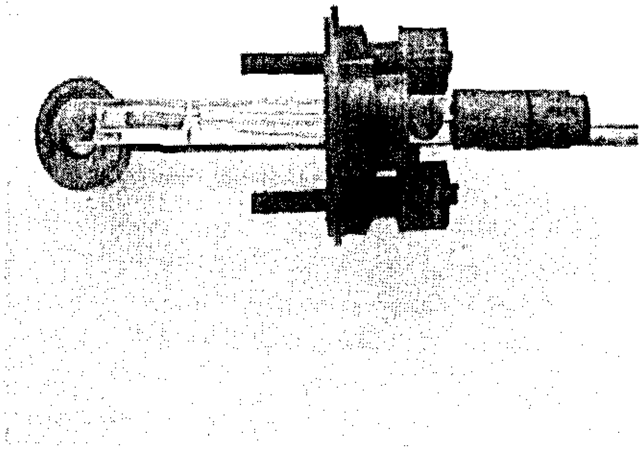
c) The **third probe (PVC.Carb.RE)** (Figure 2.5) consisted of a 25 - 19 mm PVC reducing bush as electrode holder. Embedded within this bush mounted in an epoxy resin were two carbon rods, one operating as a reference electrode and the other as a counter electrode. A mild steel rod, used as a working electrode with an exposed surface area of 0,665 cm^2 was also embedded into the resin.

2.1.4 Corrosion rigs

a) **Six pipe system** (Figure 2.6)
Six identical PVC pipe systems with an inside diameter 80 mm were constructed such that six removable boxes with five mild steel strip coupons each could be placed in a horizontal section. Another horizontal HDPE pipe section for nine different ECI and corrater electrode systems and a tap for draining was provided. Coupon boxes could be removed from a vertical stand pipe.

Water was recycled through each pipe system with a small submersible pump (Little Giant Model 5 MSP) from a 200 ℓ plastic container.

b) **Two pipe system** (Figure 2.7)
The two pipe system was based on a rig as described by Williams (1984) but consisted of two 150 mm ID PVC through-flow pipes. In these pipes provision were made for slide coupons and reducing bush type ECI electrode systems as well as for corrater electrodes. Water was recycled from a 200 ℓ plastic container with a Little Giant Model 5-MSP, submersible pump.



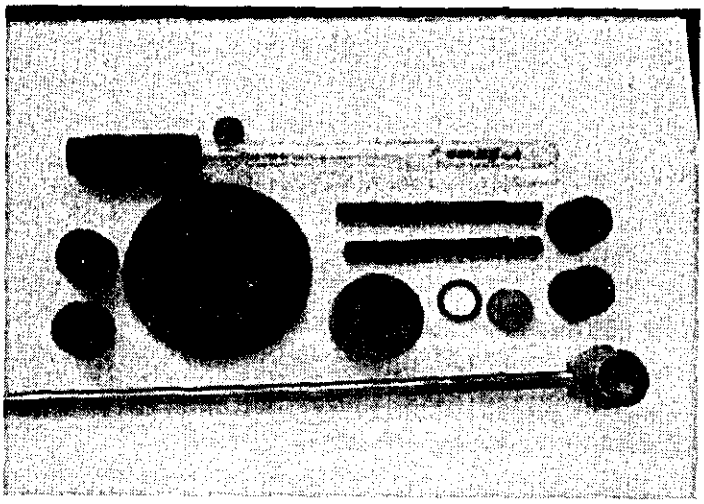


FIGURE 2.3 PROBE WITH CALOMEL ELECTRODE WITHOUT LUGGIN CAPILLARY (CALO.RE)

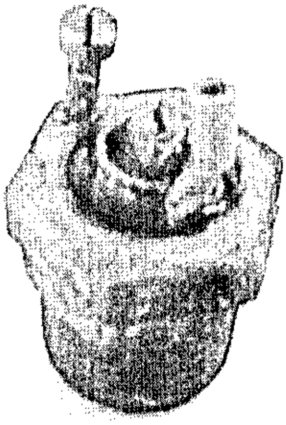


FIGURE 2.4: 19mm GALVANISED PROBE WITH MILD STEEL REFERENCE AND CARBON COUNTER ELECTRODE (MILD S.RE).

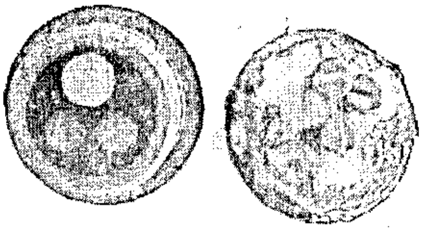
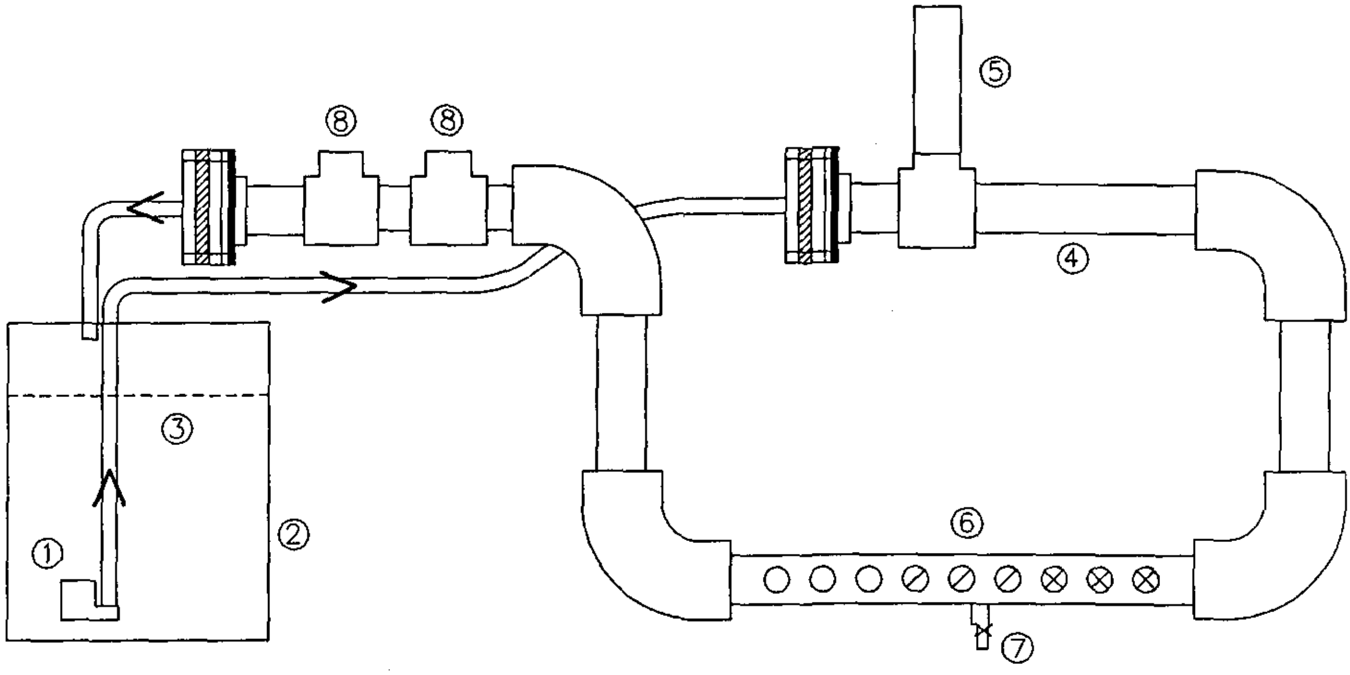


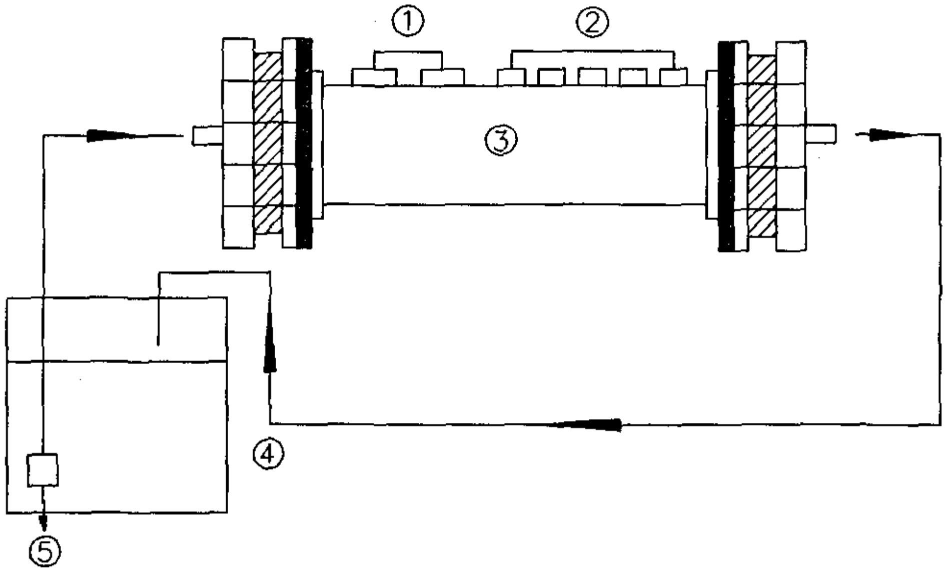
FIGURE 2.5: 19mm PVC PROBE WITH CARBON REFERENCE AND COUNTER ELECTRODES (PVC.CARB.RE)



① Submersible pump
② 200 liter container
③ 100 liter water
④ 1meter 80mm ID PVC pipe with eight coupon holders each with five mild steel coupons; 74mm x 30mm x 1,2mm
⑤ Opening through which coupons holders can be removed
⑥ 1 meter HDPE 80mm ID pipe with nine positions for ECI electrode systems
⑦ Drain tap
⑧ Openings for Calo RE

Figure 2.6 Design of six pipe system with sections for ECI electrode systems,corrator electrodes and mild steel coupons

CAD335M



① Position for Calo. RE systems

② Position for Carb. PVC. RE systems and corrater electrodes

③ 1 meter 150mm ID PVC pipe that can also contain mild steel coupon holders

④ 200l container

⑤ Submersible pump

Figure 2.7 Design of a two pipe system with positions for ECl and corrater electrodes and containing coupon holders

CAD335L

2.1.5 Mild steel strip coupons

Mild steel strip coupons (75 x 30 x 1 mm) were used throughout the investigation. The method followed for the preparation and handling of the coupons before and after corrosion tests complied with the ASTM standard practice (ASTM, 1972). Coupons were prepared as detailed in paragraph 2.2.1. General chemical composition is shown in Table 2.1c.

TABLE 2.1c: GENERAL CHEMICAL COMPOSITION OF MILD STEEL COUPONS.

Supplier: Iscor (Ltd) Vanderbijlpark.
Mild steel plates as rolled for strip coupons and rods

CHEMICAL ANALYSIS				
C %	Mn %	P %	S %	Si %
0,20	1,02	0,012	0,02	0,11

2.1.6 Oxygen measurements

Oxygen measurements were made with a WTW OXI 196 Micro processor Oximeter. This instrument was standardised in deionised water saturated with oxygen at 23-24°C and 643 mm Hg barometric pressure.

2.1.7 pH measurements

The pH was determined with a Metrohm pH meter, Model 654.

2.1.8 Conductivity measurements

Conductivity was measured with a WTW D8120 Weilheim conductivity meter.

2.2 PREPARATION AND HANDLING OF COUPONS AND WORKING ELECTRODES

2.2.1 Coupon strips

All the mild steel strip coupons were cut from sheets of 1 mm metal plate using an industrial metal cutting guillotine. Rough edges of the coupons were removed with grinding paper, where after they were glass blasted with 500 grid glass beads to obtain clean uniform surfaces. The coupons were then dipped into a hydrochloric acid base rust remover (Hibitex[1], obtainable from Protea (Pty) Ltd) for a few seconds, rinsed in

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[1] Hibitex contains an inhibitor with trade name armahib.

tap water, and dried with a paper cloth. The mean mass loss of ten unused coupons left in Hibitex for the same period as for used coupons with rust layer was 0,028%. This was found to be equivalent to about 4% of mass loss due to the corrosion process. After this procedure the dimensions of the coupons were determined as follows:

Five measurements of respectively the length and width of each coupon were done with a vernier with an accuracy of 0,05 mm. Five measurements of the thickness were done with a micrometer, with an accuracy of 0,01 mm. The results were expressed in mm. The mass in grams was determined on a four decimal electronic balance.

Coupons were then degreased in acetone for a few seconds and dried with a paper towel and compressed air.

After the coupons had been exposed in a corrosive medium the same procedure as discussed above was followed to remove the rust, whereafter the mass was again determined. From the difference between the initial mass and mass after exposure, the corrosion rates were determined as discussed in paragraph 2.6.1.

2.2.2 Preparation of working electrodes

The surfaces of all working electrodes were polished on a Jean Wirtz Model TG200 grinding machine using 180 and 1200 grit water sandpaper in succession. After polishing the electrodes were degreased with acetone and stored in a desiccator.

All corrosion measurements for the laboratory investigation were done with uniformly corroded working electrodes. For this purpose the working electrodes were left in deionised water for 20 hours. Only working electrodes that were uniformly corroded, without pitting, were used.

For investigation done on the through flow systems all working electrodes were used immediately after polishing of the surface areas.

2.3 LABORATORY INVESTIGATION

2.3.1 Chemicals and stock solutions

All the chemicals used for altering or adjusting the chemical composition of water samples and degreasing of coupons were of analytical grade. Mainly Sterkfontein Dam water was used for the investigation because of it's relative purity, thus preventing to a great extent the effect of other substances on the corrosion process.

2.3.2 Water samples used as electrolytes

After adjusting the chemical composition, samples were saturated with oxygen at a temperature of 23 - 24°C and atmospheric pressure of ± 643 mm Hg to between 96 and 98% of saturation resulting in an oxygen content of between 6,9 and 7,0 mg/ℓ.

The pH was then adjusted to the required value with sodium hydroxide or nitric acid after which the conductivity of the samples was measured. Prepared electrolytes were stored in plastic containers, filled to the rim, and sealed to prevent oxygen from escaping. The electrochemical cell consisted of a 500 cm^3 glass beaker, a magnetic stirrer and the working electrodes clamped in a fixed position. Just before producing the Tafel Plot the lid of the container was removed, the beaker filled to the 500 cm^3 mark with the sample, and the stirrer switched on. The E_{corr} reading on the monitor was allowed to stabilise before commencing with the experiment and by changing the potential, allowing the Tafel Plot to be drawn.

2.4 THROUGH FLOW SYSTEM INVESTIGATION

Where the effect of different chemicals were examined in the through flow systems the chemical composition of the water, before the addition of specific chemicals, was adjusted to give an alkalinity of 80 mg/ℓ $CaCO_3$ and pH of 8,2. Calcium bicarbonate at pH 6,0 and calcium hydroxide were used. Neat Sterkfontein Dam water was used as reference in the six pipe system .

The calcium bicarbonate solution was prepared by over saturating Sterkfontein Dam water in 20ℓ glass bottles with calcium carbonate laboratory reagent. Hereafter carbon dioxide was bubbled through the solution under pressure until a pH $\approx$ 6 was obtained. The mixture was left until all the supernatant was clear after which the calcium and alkalinity content were determined. With known calcium and alkalinity content different dosages were calculated accordingly.

2.5 MEASURING PROCEDURES

2.5.1 Through flow system

The linear flow rate in the two pipe system was 5 m/min and in the six pipe system 9 m/min. Working electrodes were positioned such that their flat surfaces were parallel to the flow direction of the sample. The electrodes of the corrater were placed so that the two points were perpendicular to the flow of the sample.

2.5.2 Linear Polarization technique

The electrochemical corrosion rate measurements for each water sample in a set was compared to that obtained for a reference standard with chemical composition corresponding to the mean chemical composition of the set. After the corrosion rate of each sample in a set had been measured, the corrosion rate in the reference standard was measured as well. The corrosion rate of the sample was then corrected by the same percentage deviation the reference standard deviated from the mean value of all the corrosion rate measurements in a standardised electrolyte. The deviations from the mean corrosion rate obtained in the standard solutions are shown in Tables 2.2, 2.3 and 2.4 as examples.

To eliminate the formation of corrosion products that might have influenced the corrosion rate measurements on the working electrode surface, the time taken to produce Tafel Plots were kept as short as possible. This was achieved by:

a) Completing all measurements for each set of samples and reference standard, first with one type of electrochemical electrode, followed by the next type, etc.

b) Completing all measurements for each set of samples during an 8 hour period (1 day).

c) Using a high sweep rate that would still ensure a reliable Tafel Plot. For this investigation a sweep rate of 1V/min and completion time of 1,25 min were used throughout.

TABLE 2.2

DEVIATION OF MEASURED CORROSION RATES OBTAINED WITH THE CALO.RE FROM THE MEAN CORROSION RATE.

(REFERENCE SOLUTION)

CORROSION RATE µm/y	DEVIATION FROM MEAN VALUE %
471	-7,99
474	-7,44
464	-9,28
475	-7,19
528	+3,23
516	+0,74
523	+2,23
538	+5,21
546	+6,99
528	+3,23
536	+4,72
551	+7,69
489	-4,52
549	-7,20
498	-2,73
503	-1,74
Mean 513 ± 43	

TABLE 2.3

DEVIATION OF MEASURED CORROSION RATES OBTAINED WITH THE MILD S.RE FROM THE MEAN CORROSION RATE.

(REFERENCE SOLUTION)

CORROSION RATE μm/y	DEVIATION FROM MEAN VALUE %
2809	-14,88
2665	-19,24
3828	+18,04
3398	+2,96
3450	+4,54
3378	+2,36
3322	+0,68
3532	+7,02
3208	-2,79
3116	-13,29
2685	-18,65
2616	-20,73
4404	+32,69
4049	+22,67
3627	+9,90
2996	-9,23
Mean 3299 ± 894	

TABLE 2.4

DEVIATION OF MEASURED CORROSION RATES OBTAINED WITH THE PVC.CARB.RE FROM THE MEAN CORROSION RATE.

(REFERENCE SOLUTION)

CORROSION RATE μm/y	DEVIATION FROM MEAN VALUE %
498	-10,22
542	-2,34
554	-0,09
549	-1,05
528	-4,72
527	-4,90
603	+8,70
556	+0,32
579	+4,43
592	+6,70
541	-2,43
535	-3,53
604	+8,98
571	+3,02
581	+4,72
512	-7,70
Mean 554 ± 53	

2.6 CALCULATIONS

2.6.1 Coupons

A computer program was developed to calculate the mean of the various physical dimensions and mass of the strip coupons, as well as the mass loss. In all cases the average deviation, variance and standard deviation was also determined (Bauer, 1971).

By using the above data, the corrosion rate was then calculated using the equation (ASTM, 1988).

Corrosion rate $\mu m/y = (k_1 \times w)/(A_1 \times T_1 \times d)$ . . . . (2)

Where

k_1 = $8{,}76 \times 10^7$ for micrometers per year ($\mu m/y$).
T_1 = exposure time in hours to the nearest 0,01h.
A_1 = area in cm^2 to the nearest 0,01 cm^2.
w = mass loss in g, to the nearest 1 mg.
d = density in g/cm^3.

The density of mild steel used for the strip coupons was 7,70375 g/cm^3.

2.6.2 Working electrodes

From the Tafel Plots the corrosion rates were calculated as follows. At values of 400 to 500 mV greater than the E_{corr} value, five tangents to the graphs were drawn. This method was adapted because the anodic Tafel Plots were somewhat curved with a linear relationship obtained between the slopes and I_{corr} values for different tangents to the curve. The Tafel Slope and I_{corr} value for each tangent were fed into a Sharp scientific calculator EL-5103S to determine with two variable statistics and linear regression, the equation for a straight line of the type

$$y = a + bx$$

with x equal to I_{corr} and y equal to the Tafel Slope. The equations were only accepted if the correlation coefficient (r) between I_{corr} and the Tafel Slope exceeded 95%. From these equations I_{corr} values for Tafel Slopes of 600 mV/decade were then calculated. This procedure was followed for all samples, and a Tafel Slope of 600 mV/decade was used throughout. The calculated I_{corr} values were then substituted into the equation.

$$\mu m/y = \frac{11{,}23 \times I_{corr}}{A} \quad \ldots \quad (3)$$

Where

A = surface area of working electrode in cm^2.

Equation (3) derives from the following equation (Publication of the National Association of Corrosion Engineers, 1972):

$$\text{Corrosion rate (mpy)} = \frac{0.13\, I_{corr}\, E}{d}$$

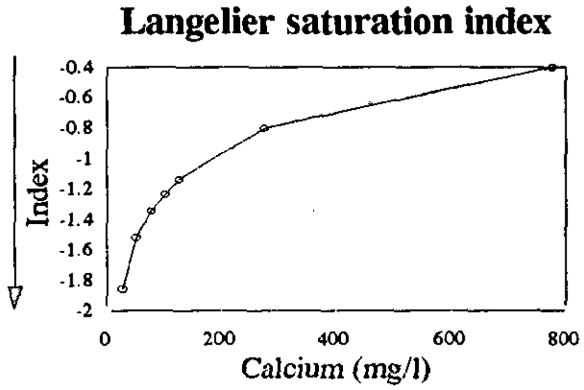
Where

E = equivalent weight of mild steel, g.
d = density of the corroding species, g/cm^3.
I_{corr} = corrosion current density, μA/cm^2.
mpy = mils per year.

For converting corrosion rates from mpy to μm/y, the equation above is multiplied by 25,4 to give equation (3).

2.7 GRAPHICAL PRESENTATION OF THE INDICES VALUES

In the graphical representations of the indices values (ordinates), the arrows next to the Index value axis indicate the direction of increasing corrosivity. See example below:-



3. RESULTS OF LABORATORY STUDIES

3.1 COMPARISON OF CORROSION RATES WITH CALCULATED INDICES VALUES (Ca) FOR VARIOUS ANIONS AND ONE CATION IN STERKFONTEIN DAM WATER MEASURED WITH A CORRATER (PRELIMINARY INVESTIGATION).

3.1.1 Increasing concentration of chloride, sulphate, calcium and alkalinity at pH 7,0

Only seven graphs are presented. The Ryznar Stability Index (RSI) values (Figure 3.1) show the same tendency as the corrosion rates measured for increasing chloride concentration as shown in Figure 3.5. While the Riddick Corrosion Index (RCI) (Figure 3.2) corresponded only partly with the corrosion rates measured for increasing chloride concentration. Corrosiveness predicted by the Langelier Saturation Index (LSI) (Figure 3.3) versus increasing calcium concentration were the opposite to tendencies obtained by the actual measured corrosion rates (Figure 3.6) at increasing calcium concentrations. The Aggressive Index (AI), Figure 3.4, showed no sensitivity towards increasing sulphate concentration while the actual corrosion rates showed a possible relationship with sulphate concentration. (Figure 3.7.) In Table 3.1 the calculated indices and measured corrosion rates are compared. From these results it may be concluded that the indices, except for the Feigenbaum (Y) and Aggressive (AI) indices, predicted increasing corrosiveness for increasing chloride and sulphate concentrations and thus coincided with the measured corrosion rates. In relation to increasing calcium concentration all indices, except for the Riddick Corrosion Index (RCI) and Larson Index (LI), predicted patterns that were opposite to the tendencies obtained for the measured corrosion rates. The RCI values increased with higher concentration while the LI showed no sensitivity towards increasing calcium concentration.

TABLE 3.1 COMPARISON OF CALCULATED INDICES TENDENCIES WITH MEASURED CORROSION RATE TENDENCIES.

INDEX	CHLORIDE	SULPHATE	CALCIUM	ALKALINITY*
RSI	S	S	O	O
LSI	S	S	O	O
AI	-	-	O	O
DFI	S	S	O	O
RCI	S'	O	S	O
LI	S'	S'	-	O
CI	S'	S'	O	S'
Y	O	O	O	O

*	Alkalinity as $CaCO_3$	S	Similar tendency as the measured corrosion rates
S'	Partly similar	-	Show no sensitivity
O	The opposite tendency as the measured corrosion rates		

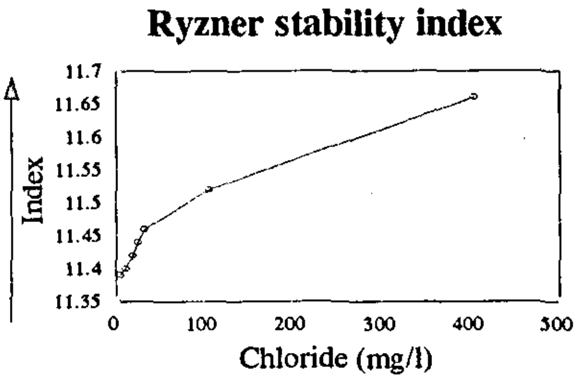


FIGURE 3.1

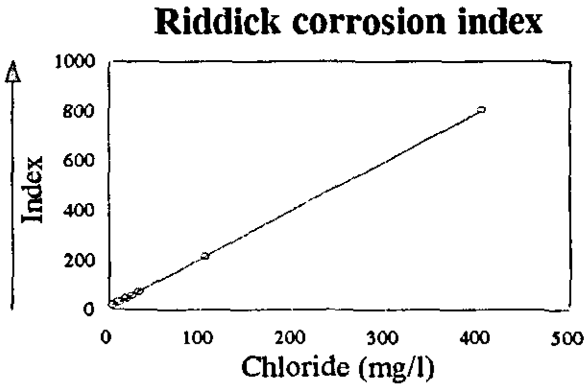


FIGURE 3.2

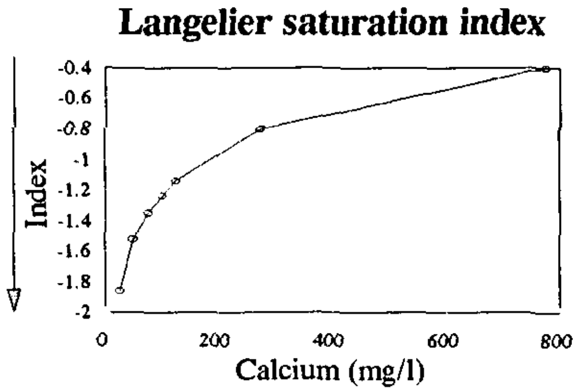


FIGURE 3.3

FIGURE 3.1 TO 3.3 **CALCULATED INDICES VALUES VERSUS INCREASING CONCENTRATIONS OF CHLORIDE AND CALCIUM AT pH7.**

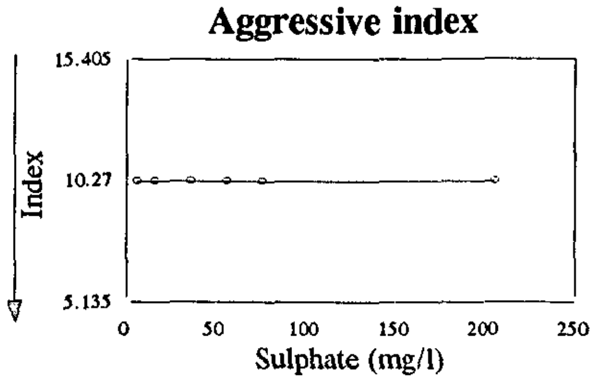

Aggressive index

FIGURE 3.4

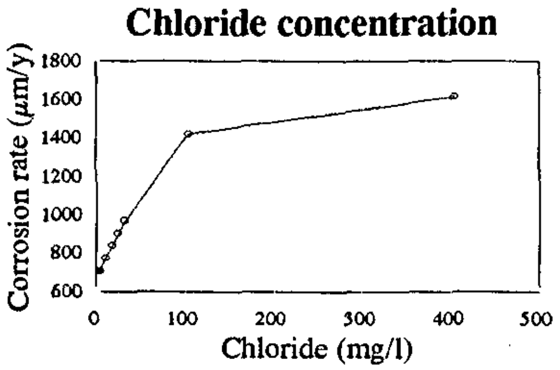

Chloride concentration

FIGURE 3.5

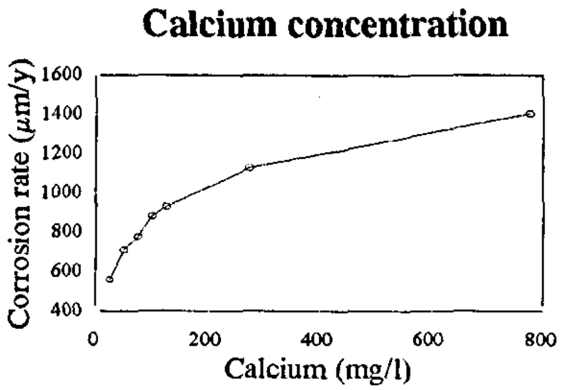

Calcium concentration

FIGURE 3.6

FIGURES 3.4 TO 3.6: **CORROSION RATES AND CALCULATED INDICES IN STERKFONTEIN DAM WATER FOR INCREASING CONCENTRATIONS OF SULPHATE, CHLORIDE AND CALCIUM AT pH7.**

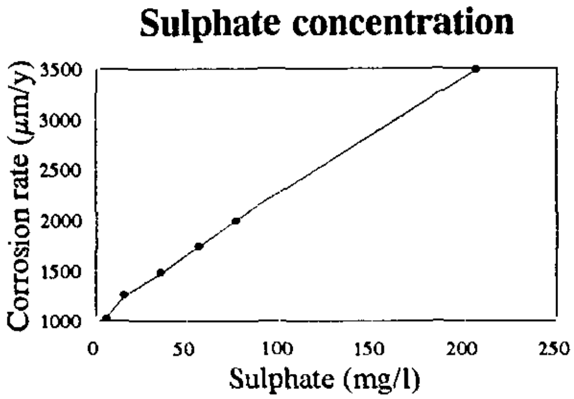


FIGURE 3.7: CORROSION RATES FOR INCREASING CONCENTRATION OF SULPHATE IN STERKFONTEIN DAM WATER AT pH 7.

3.1.2 Different Cl^-/SO_4^{2-} ratios at pH 7,0

The effect of different chloride/sulphate ratios on the corrosion rate and calculated indices in Sterkfontein Dam water are shown in Figures 3.8, 3.9 and 3.10 respectively. The tendencies for the measured corrosion rates are not prominent because of the wide range of Cl^-/SO_4^{2-} ratios. A graph with the measured and calculated values versus log Cl^-/SO_4^{2-} shows the tendencies more clearly. The analysis of some of the adjusted Sterkfontein Dam water samples are shown in computer printouts 1 and 2. In Figure 3.8 it can be seen that the corrosion rate is lower at a high chloride to sulphate ratio (high Cl^- concentration) on the left hand side of the graph, while it is higher at low chloride to sulphate ratio (high sulphate concentrations) on the right hand side of the graph. This same tendency is noticeable for the Larson and Cassil Indices, as can be seen in Figures 3.9 and 3.10 but not for the other indices.

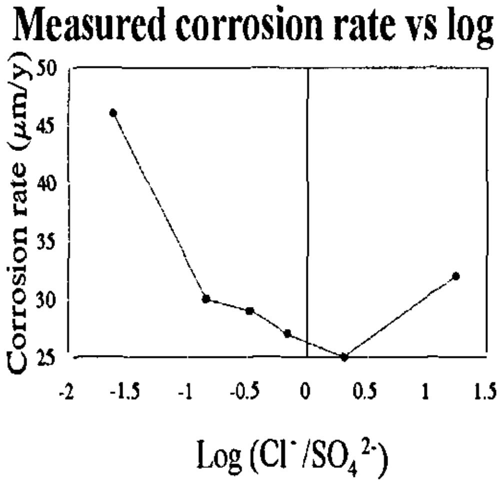


FIGURE 3.8

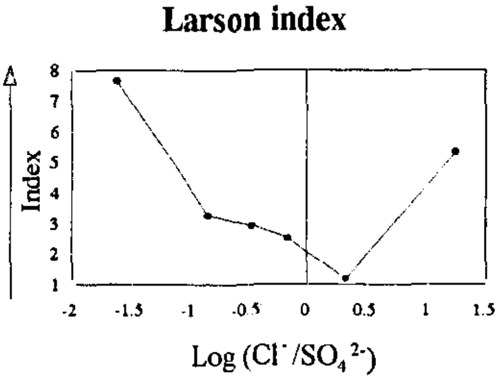


FIGURE 3.9

FIGURES 3.8 AND 3.9 MEASURED CORROSION RATES AND CALCULATED INDICES VALUES VERSUS THE LOGARITHM OF DIFFERENT CHLORIDE TO SULPHATE RATIO'S AT pH 7.

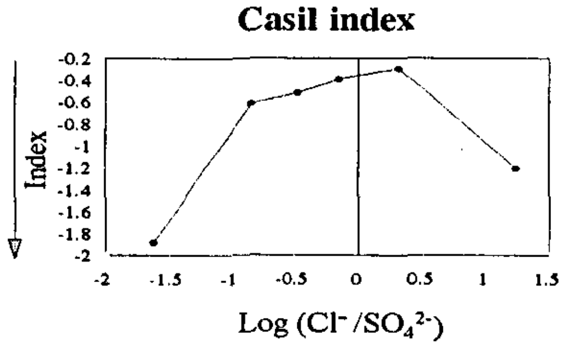


FIGURE 3.10: CALCULATED INDICES VALUES VERSUS THE LOGARITHM OF DIFFERENT CHLORIDE TO SULPHATE RATIO'S AT pH 7.

3.2 COMPARISON OF THE CORROSION RATE MEASUREMENTS FOR VARIOUS ELECTROCHEMICAL ELECTRODES AND SURFACE CONDITIONS OF THE WORKING ELECTRODES

In this investigation two types of ECI electrochemical electrodes and the corrater electrodes were compared to determine which type gave the most reliable results. Parallel to this investigation, the effect of the state of corrosion of the working electrodes and corrater electrodes were compared. The one ECI electrode configuration consisted of a disc working electrode with a calomel electrode (Calo.RE) without Luggin capillary, and two carbon counter electrodes (Figure 2.4). The second ECI electrode configuration consisted of a 19 mm galvanised reducing bush with ring type working electrode and mild steel reference electrode (Mild S.RE) (Figure 2.5).

The surface conditions of the working electrodes and corrater electrodes (see discussion in paragraph 2.2) that were compared were:-

- corroded
- corroded and then treated with Hibitex and acetone to remove rust and grease
- polished working electrode surfaces

The chemical composition of the samples that were used for this investigation are given in Table 3.2. In Figures 3.11 to 3.13 the corrosion rate measurements versus log Cl^-/SO_4^{2-} ratios are shown separately for each electrochemical cell and the three different corroded conditions of the working electrodes.

As was discussed in paragraph 3.1.2 the measured corrosion rates correlate with the calculated Larson Index values for increasing Cl/SO_4^{2-} ratios. In this investigation the same tendencies were observed, as can be seen in Figures 3.11, 3.12 and 3.13, as well as in Figures 3.14 and 3.15. In the latter two figures the Larson Index and the total dissolved solids concentration versus log Cl/SO_4^{2-} are shown graphically.

Measured corrosion rates with corroded working electrode compared to the log Cl^-/SO_4^{2-} showed the same pattern as the LI and TDS vs log Cl/SO_4^{2-}. From the tendencies shown in Figures 3.11, 3.12 and 3.13, those for the corroded working electrodes correlate favourably with the tendencies as shown for the Larson Index and dissolved solids in Figures 3.14 and 3.15. Corrater electrodes that were polished, corroded and from which rust had been removed, showed the same tendencies. The same observation applies for the Calo.RE, but for the Mild S.RE only the corroded working electrode showed the same tendency. In conclusion it can be said that the most reliable corrosion rate determinations would be obtained with uniformly corroded electrodes.

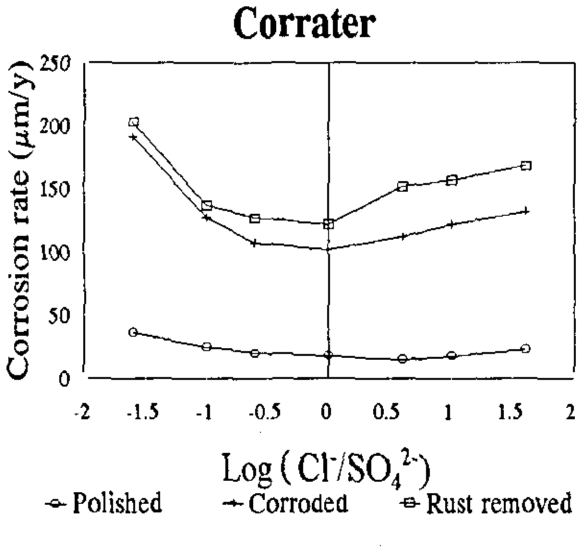


FIGURE 3.11: COMPARISON OF THE CORROSION RATE MEASUREMENTS FOR VARIOUS ELECTROCHEMICAL ELECTRODES AND SURFACE CONDITIONS OF THE WORKING ELECTRODES VERSUS THE LOGARITHM OF DIFFERENT CHLORIDE TO SULPHATE RATIO'S AT pH 10.

TABLE 3.2

CHEMICAL COMPOSITION OF SAMPLES WITH DIFFERENT $C\ell^-/SO_4^{2-}$ RATIOS AT pH 10

C1/SO4^{2-} ratio	0,025	0,100	0,250	1,0	4,0	10,0	40,0
mg SO4^{2-}/ℓ	200	100	80	40	20	10	5
mg C1$^-$/ℓ	5	10	20	40	80	100	200
mg Na$^+$/ℓ	90,03	54,37	51,28	45,08	61,42	69,59	131,99
Alkalinities as mg CaCO3/ℓ	10,0	10,0	10,0	10,0	10,0	10,0	10,0
Dissolved solids TDS mg/ℓ	304,00	164,37	165,08	125,08	161,42	179,59	331,99
Conductivity mS/m	45,24	24,41	24,41	18,61	24,05	26,73	49,40
Ionic strength	0,00760	0,00410	0,00313	0,00404	0,00449	0,00830	

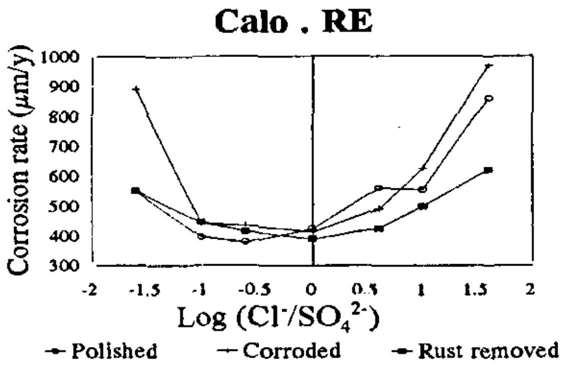


FIGURE 3.12

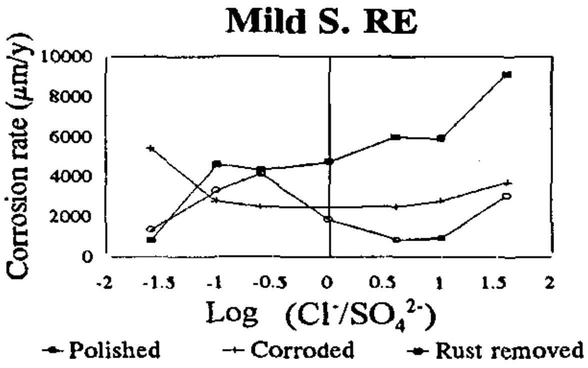


FIGURE 3.13

FIGURES 3.12 AND 3.13: COMPARISON OF THE CORROSION RATE MEASUREMENTS FOR VARIOUS ELECTROCHEMICAL ELECTRODES AND SURFACE CONDITIONS OF THE WORKING ELECTRODES VERSUS THE LOGARITHM OF DIFFERENT CHLORIDE TO SULPHATE RATIO'S AT pH 10.

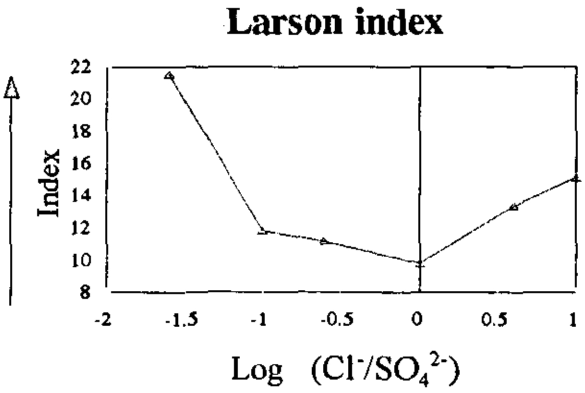


FIGURE 3.14

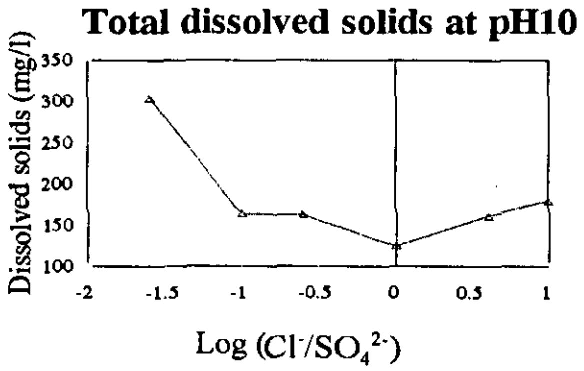


FIGURE 3.15

FIGURE 3.14 AND 3.15: THE LARSON INDEX VALUES AND DISSOLVED SOLIDS VERSUS THE LOGARITHM OF DIFFERENT Cl^-/SO_4^{2-} RATIO'S AT pH 10.

3.3 REPEATABILITY OF CORROSION RATE MEASUREMENTS

3.3.1 Repeatability

The repeatability of the corrosion rate measurements for the Calo.RE, Mild S.RE and corrater electrodes was determined with corroded working electrodes, by repeating the measurements ten times. The chemical composition of the sample used for this investigation was as follows:

Deionised water containing:
50 mg/ℓ Na_2CO_3
50 mg/ℓ $Ca(NO_3)_2$
6,9 mg 0_2/ℓ, 95% saturation
pH = 9,7

The corrosion rate measurements as well as their statistical evaluation are shown in table 3.3. The standard deviations from the mean corrosion rates show that the repeatability with the corrater was slightly better than that for the Calo.RE, whilst for the Mild S.RE, it was the worst.

TABLE 3.3: STATISTICAL EVALUATION OF REPEATABILITY OF CORROSION RATE MEASUREMENTS WITH CORRATER, CALO.RE AND MILD S.RE

Working Electrode	Mean μm/y	Mean Deviation	Variance	Standard Deviation	% Standard Deviation
Corrater	19,8	0,9	0,05	1,0	5,13
Calo.RE	2368	153	1227	177	7,46
Mild S.RE	9,1	4,0	0,9	4,8	44,44

Mean μm/y = x; Mean deviation = $\frac{\underline{(x - x)}}{n}$; variance = $\Sigma(x - x)^2/n\text{-}1$;

Standard deviation = $\Sigma(x\text{-}x)^2/n\text{-}1\ ^{1/2}$;

% Standard deviation = $\frac{\frac{\Sigma(x - x)^2}{n - 1}^{1/2} \times 100}{x}$

3.3.2 *Other factors influencing the reliability of corrosion rate measurements*

At this point during the investigation a number of other factors concerning the corrosion rate measurements came to light. These are:

a) The time delay between the measurements of different samples must be as short as possible, because if it is too long (one day) the corrosion condition of the working electrodes can change to such an extent that misleading results are possible.

b) The time taken to complete a Tafel Plot must be as short as possible to prevent drastic changes in the state of corrosion of the working electrodes.

c) All corrosion rate measurements must be measured against a standard reference solution so as to eliminate deviations that may occur because of the corrosion state of the working electrodes.

3.4 CORROSION RATES OF DIFFERENT $C\ell/SO_4^{2-}$ RATIOS AND DIFFERENT CONDUCTIVITY LEVELS AT pH 10.

In this investigation a third type of ECI-electrochemical electrode system developed by Rand Water was tested. This electrode, consisting of a PVC reducing bush (Figure 2.6) and a carbon reference electrode, is fully discussed in paragraph 2.1.4.

The corrosion rates were measured with a Calo.RE, a PVC.Carb.RE, a Mild S.RE electrode and a corrater. A set of four samples, with $C\ell/SO_4^{2-}$ ratios of respectively 0,025, 0,25, 4,00 and 40,00, chemical composition as shown in Table 3.2 and conductivities of respectively 43, 24, 30 and 57 mS/m were used. The measurements were repeated, but the conductivity for each set adjusted to 57, 70 and 100 mS/m with sodium acetate (NaAc).

The results obtained with the respective electrodes are presented graphically in Figures 3.16 to 3.19. The conductivity values for the samples versus log $C\ell^-/SO_4^{2-}$ are shown in Figure 3.20.

An important observation from this investigation was firstly that the corrosion rates in various electrolytes followed the same trends as the conductivity values, where the conductivity of electrolytes were adapted to constant values the corrosion rates measured were also constant (irrespective of the chemical composition). Secondly the most reliable measurements were obtained with the corrater, Calo.RE and PVC.Carb.RE, working electrodes while the results obtained with the Mild S.RE were the most unreliable.

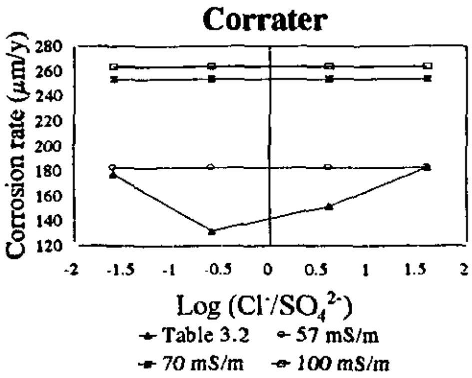


FIGURE 3.16

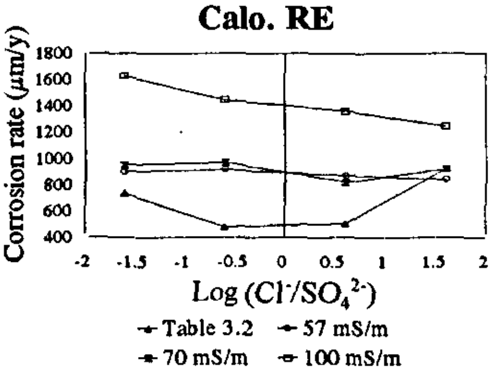


FIGURE 3.17

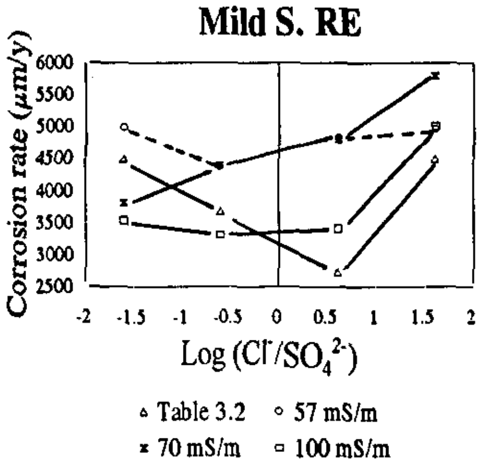


FIGURE 3.18

FIGURES 3.16 TO 3.18 CORROSION RATES FOR DIFFERENT Cl^-/SO_4^{2-} RATIO'S AND DIFFERENT CONDUCTIVITY LEVELS AT pH 10.

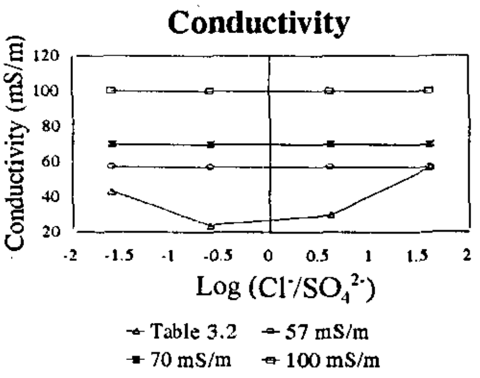


FIGURE 3.19: CORROSION RATES FOR DIFFERENT Cl^-/SO_4^{2-} RATIO'S AND DIFFERENT CONDUCTIVITY LEVELS AT pH 10.

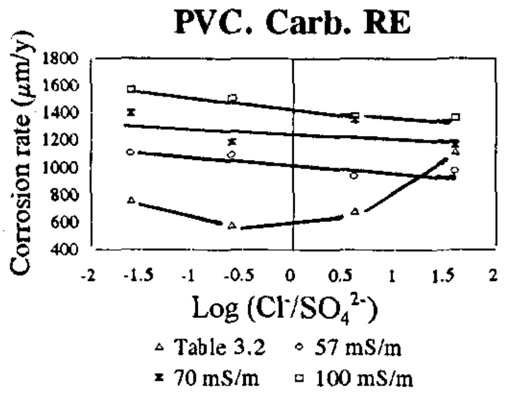


FIGURE 3.20: CONDUCTIVITY VALUES FOR DIFFERENT Cl^-/SO_4^{2-} RATIO'S AND DIFFERENT CONDUCTIVITY LEVELS AT pH 10.

3.5 THE EFFECT OF VARIOUS DETERMINANTS AND CONCENTRATIONS THEREOF ON THE CORROSION RATE OF MILD STEEL.

3.5.1 Chloride, sulphate, nitrate, bicarbonate, carbonate and hydroxide

With the results reported in paragraph 3.4 it appeared as though a direct relationship might exist between the corrosion rates and the conductivity of the samples. With this in mind, it was decided to investigate the effect of the various determinants separately. The determinants being chloride ($C\ell^-$), sulphate (SO_4^{2-}), nitrate (NO_3^-), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and hydroxide (OH^-). The pH of all the samples were adjusted to 10, except for bicarbonate, carbonate and hydroxide. To ensure that alkalinity of only the desired species were present, the pH had to be adjusted as follows: to pH 8,3, to ensure that alkalinity would be present as bicarbonate (HCO_3^-), and to pH 12, to have all alkalinity present as predominantly carbonate (CO_3^{2-}). The desired concentration levels of hydroxide (OH^-) was achieved by adjusting the pH with sodium hydroxide and nitric acid. Concentration levels of the different determinants, excluding OH^-, varied from 10 to 480 mg/ℓ.

This investigation was done with the Calo.RE and repeated with the PVC.Carb.RE and corrater. Results can be seen in detail description, Addendum D tables D1 to D4.

The corrosion rate results are graphically represented for only the Calo.RE in Figures 3.21 and 3.22 for bicarbonate and pH respectively. Change in conductivity as a result of changes in bicarbonate concentration and pH are graphically represented in Figures 3.23 and 3.24.

The corrosion rates as well as the conductivities increases linearly with increasing concentration for the various chemical species. For increasing pH the conductivity and corrosion rates increased logarithmically for pH higher than 10. The anodic plot indicated an increasing tendency for passivation from pH 10 to 13. and for this reason the calculated corrosion rates as calculated from the tangent ot the anodic plots may be misleading (Figure 3.22 and 3.24). For al the other measuring techniques the same tendencies as for the Calo.RE were observed and for this reason are not graphically represented here. First order equations for the linearities were formulated and are as follows:

<u>Corrosion rates as measured with the Calo.RE</u>

Chloride ($C\ell^-$) : CR = 3,20 Ce + 253 . . . . (4)
r = 0,99
Sulphate (SO_4^{2-}) : CR = 3,15 Cs + 147 . . . . (5)
r = 1,00
Nitrate (NO_3^-) : CR = 1,70 Cn + 212 . . . . (6)
r = 0,99
Bicarbonate (HCO_3^-) : CR = 2,44 Ch + 80 . . . . (7)
as $CaCO_3$) r = 0,99
Carbonate (CO_3^{2-}) : CR = 6,49 Cc + 3609 . . . . (8)
r = 0,69

Ce, Cs, Cn, Ch and Ce concentration of respectively $C\ell^-$, SO_4^{2-}, NO_3^-, HCO_3^- and CO_3^{2-} in mg/ℓ

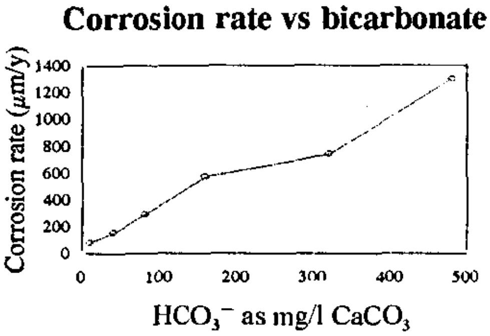


FIGURE 3.21

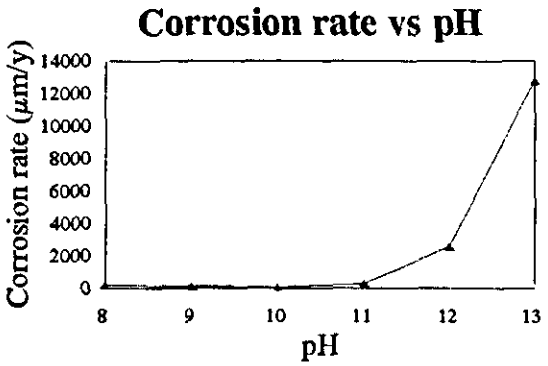


FIGURE 3.22

FIGURES 3.21 AND 3.22: CORROSION RATE VERSUS BICARBONATE CONCENTRATION AND pH INCREASE

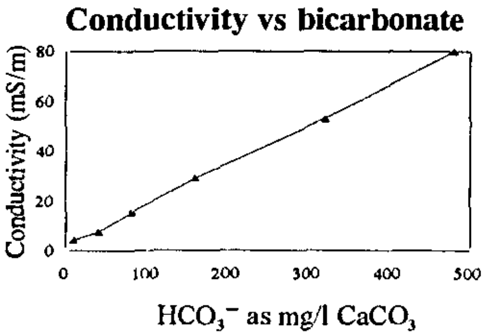


FIGURE 3.23: CONDUCTIVITY VERSUS INCREASE IN BICARBONATE CONCENTRATION.

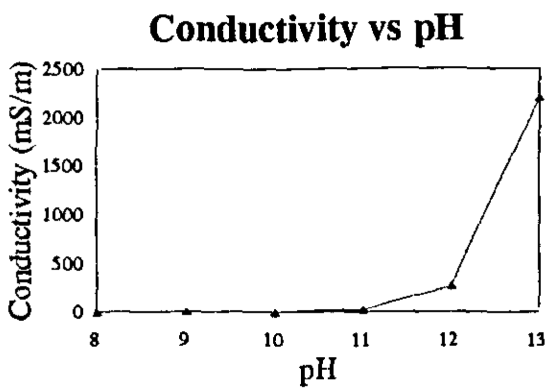


FIGURE 3.24: CONDUCTIVITY VERSUS pH INCREASE

Conductivity

Chloride ($C\ell^-$) : Con = 0,288 Ce + 2,36 .... (9)
r = 1.00
Sulphate (SO_4^{2-}) : Con = 0,194 Cs + 7,02 .... (10)
r = 1,00
Nitrate (NO_3^-) : Con = 0,149 Cn + 6,03 .... (11)
r = 1,00
Bicarbonate (HCO_3^-) as $CaCO_3$: Con = 0,161 Ch + 2,50 .... (12)
r = 1,00
Carbonate (CO_3^{2-}) : Con = -0,030 Cc + 4,85 .... (13)
r = -0,21

Where:

CR = corrosion rate in micron per year (μm/y)
C = concentration in mg/ℓ
Con = conductivity in mS/m
Ce = mg/ℓ $C\ell^-$
Cs = mg/ℓ SO_4^{2-}
Cn = mg/ℓ NO_3^-
Ch = mg /ℓ HCO_3^-
Cc = mg/ℓ CO_3^{2-}

3.5.2 Effect of Ca^{2+} ions on the corrosion rate and conductivity at pH 8,3 and pH 10 in samples containing carbonate species

Two sets of six litre electrolyte each with an increasing sodium carbonate concentration expressed as $CaCO_3$/ℓ were prepared. 50 mg Ca as $Ca(NO_3)_2$ was added to all aliquates in one set while no additional calcium as $Ca(NO_3)_2$ was added to the second set. The pH of the samples were set at 8,3 and the conductivity and corrosion rates were determined. At pH 8,3 the alkalinity content was mainly in the bicarbonate form.

The test, as described above, was repeated, but the pH of the samples were adjusted to 10. A white precipitate, most likely of calcium carbonate was observed in the samples at pH 10 when the $CaCO_3$ concentration was higher than 24,4 mg/ℓ At a pH of 8,3 no calcium carbonate precipitate could be observed. Results of conductivity and corrosion rates (Figure 3.25 to 3.28), were determined three days after the samples were prepared and can be seen in Figures 3.25 - 3.28. The curves indicated by (1) and (2) in each diagram correspond to samples respectively containing no additional Ca and additional Ca while curve (3) represents the calculated conductivity (equation 11, paragraph 3.5.1), assuming no calcium carbonate precipitated.

The additional Ca^{2+} added to the samples at pH 8,3 caused the conductivity to increase with the same amount for all samples. In samples at pH 10 with high carbonate content, the measured conductivity converge with the conductivity of samples to which no additional Ca^{2+} had been added. The difference between the measured and calculated conductivity increased as the carbonate concentration increased, indicating calcium carbonate precipitated. Because of the formation of calcium carbonate, the carbonate concentration as well as the TDS and conductivity decreased. These tendencies did not occur at pH 8,3, because the fraction of the total carbonate that exist as CO_3^{2-} is very small (≈2%), while at pH 10, it is approximately 36%.

The measured corrosion rate followed the same patterns as the measured conductivity at pH 8,3 and pH 10. This observation indicates a direct relationship between the conductivity and corrosion rate. It also shows that the precipitation of calcium carbonate reduced the corrosion rate as a result of the reduction in conductivity.

It must to be stressed that in this research the decrease in corrosion rates was not due to calcium carbonate formation on the working electrode forming a protective layer as the electrode was placed into the samples after the formation of a calcium carbonate precipitate had formed.

Conclusions drawn from this research, are that a term, containing both Talk and CCPP (in the form Talk-CCPP), has to be included in an equation used to predict corrosion rates. The CCPP can be calculated by means of the Stasoft program (Friend, 1992) or the JTG program (Merril,1990). It can also be determined in the laboratory, by using the "marble test". In the latter instance, the Talk of the sample is determined before and after the "marble test" and the difference is equal to the CCPP (Appendix H).

Only positive CCPP values will be applied in the equation, while negative CCPP values will be ignored because no precipitated $CaCO_3$ was available to dissolve. If the CCPP is positive, it will be subtracted from the Talk. A decrease in Talk, therefore indicates a decrease in the total carbonate concentration. This will result in a decrease in the conductivity and consequently a decrease in corrosiveness, which coincides with the results obtained.

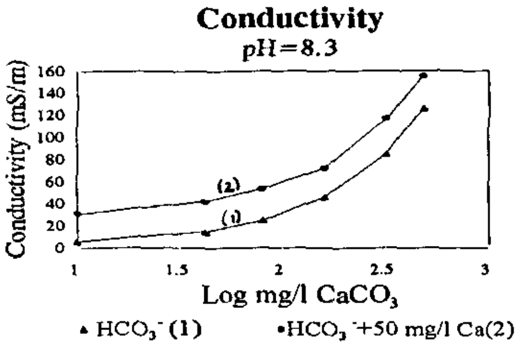


FIGURE 3.25

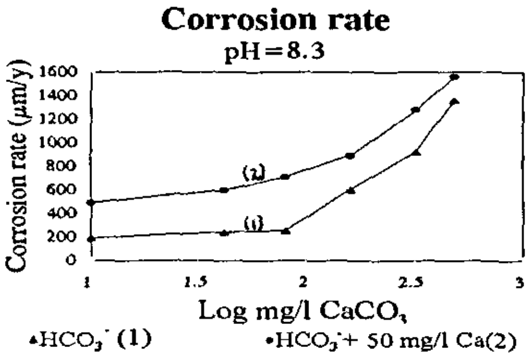


FIGURE 3.26

FIGURE 3.25 AND 3.26: CONDUCTIVITY AND CORROSION RATE VERSUS THE LOGARITHM OF INCREASING ALKALINITY WITHOUT THE ADDITION OF CALCIUM.

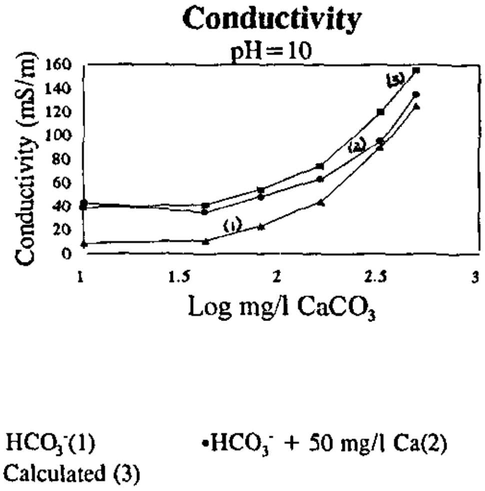


FIGURE 3.27: CONDUCTIVITY VERSUS THE LOGARITHM OF INCREASING ALKALINITY WITH THE ADDITION OF CALCIUM

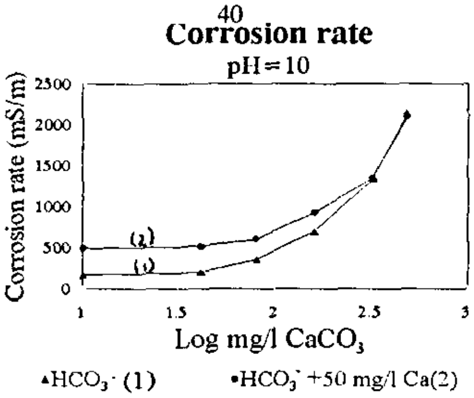


FIGURE 3.28: CORROSION RATE VERSUS THE LOGARITHM OF INCREASING ALKALINITY WITH THE ADDITION OF CALCIUM.

3.5.3 Effect of chlorine on the corrosiveness and conductivity of deionized water at pH 9,5

A stock solution of chlorine was prepared by bubbling chlorine gas through deionized water. Samples containing 1,62; 3,25; 6,5; 16,25 and 32,5 mg Cl_2/ℓ were prepared from this solution and the pH was increased to 9,5 with sodium hydroxide in each case. At this pH approximately 98% of all the chlorine will be in the hypochlorite form. The conductivity and corrosion rates were determined. The results are shown in Table 3.4.

Results indicate that there is a linear relationship between chlorine concentration and conductivity as well as the corrosion rate in the chlorine solution. These relationship can be described by the equations:

for conductivity and the corrosion rate

$$\text{Con} = 0{,}35 \text{ mg } Cl_2/\ell + 3{,}0 \quad \ldots\ldots \quad (14)$$

(regression coefficient r = 1,0)

$$\text{CR} = 5{,}46 \text{ mg } Cl_2/\ell + 55{,}1 \quad \ldots\ldots \quad (15)$$

(regression coefficient r = 1,0)

A term derived from the equation for corrosiveness versus chlorine concentration can thus be incorporated into the corrosion equation.

TABLE 3.4 CONDUCTIVITY AND CORROSION RATES OF DEIONISED WATER WITH INCREASING CHLORINE CONCENTRATION (mg Cl_2/ℓ) AT pH 9,5.

mg Cl_2/ℓ	1,625	3,25	6,5	16,25	32,5
mS/m	4,0	3,8	5,2	9,0	14,5
μm/y	74	63	89	145	233

3.5.4 Effect of oxygen content on the conductivity and corrosion rate of deionised and Sterkfontein Dam water

Only one litre samples of deionised water and Sterkfontein Dam water were used in this investigation. All the dissolved oxygen was removed by bubbling nitrogen gas through the sample, until a zero reading for oxygen content was obtained.

Oxygen was then bubbled through the sample, to produce a specific reading for the oxygen content. The container was sealed off and the corrosion rate of the sample determined with the Calo.RE electrode configuration.

Results are given in Table 3.5. The increase in corrosion rate is directly proportional to the oxygen concentration. A linear relationship was observed between the corrosion rate and oxygen concentration and the relation can be described by the equation.

$$CR = 0{,}12\,(\%0_2) + 10{,}7 \quad \text{(16)}$$

(regression coefficient r = 0,96).

The relationship between corrosion rate and oxygen content in Sterkfontein Dam water can be described by a linear or quadratic equation. This may be due to the fact that it was difficult to keep the concentration at low oxygen levels constant. Results are shown in figure 3.29. For the three highest oxygen concentrations, which gave more stable readings, a linear relationship is given by the equation.

$$CR = 0{,}12\,(\%\ 0_2) + 124 \quad \text{(17)}$$

(regression coefficient r = 0,997). The slopes for equations (16) and (17) are equal.

TABLE 3.5 CORROSION RATES FOR DEIONISED WATER WITH INCREASING OXYGEN CONTENT.

% 0_2	13	23	43	60	94
mg $0_2/\ell$	1,0	1,8	3,3	4,6	7,0
μm/y	11	15	16	17	22

TABLE 3.6: CHEMICAL ANALYSIS OF STERKFONTEIN DAM WATER (APRIL 1991)

PARAMETERS	ANALYSIS
Conductivity mS/m	9,00
Turbidity NTU	2,1
pH	6,69
pHs	8,96
Dissolved solids mg/ℓ	60,00
Alkalinity as mg $CaCO_3$/ℓ	34,00
Hardness $CaCO_3$/ℓ	32,00
Calcium mg/ℓ	8,4
Magnesium mg/ℓ	2,7
Sodium mg/ℓ	4,7
Potassium mg/ℓ	1,3
Active SiO_2 mg/ℓ	8,8
Total $Si0_2$ mg/ℓ	12,0
Nitrite mg/ℓ N	0,12
Nitrate mg/ℓ	0,21
Sulphate mg/ℓ	23,0
Chloride mg/ℓ	<10

TABLE 3.7 CHEMICAL ANALYSES OF VAAL DAM WATER (APRIL 1991)

Sample	1	2	3	4	5	6
Flocculant dosage	0	0,2	0,4	0,5	0,8	1,0
Conductivity mS/m	27	28	27	27	27	27
Turbidity NTU	17	0,57	0,22	0,29	0,26	0,28
pH	7,96	7,78	7,97	7,81	7,80	7,96
pHs	8,27	8,38	8,28	8,38	8,38	8,27
Dissolved Solids mg/ℓ	135	125	135	130	140	135
Alkalinity as mg $CaCO_3$/ℓ	92	93	91	92	91	92
Hardness as $CaCO_3$/ℓ	91	91	91	91	91	91
Calcium mg/ℓ	20	20	20	20	20	20
Magnesium mg/ℓ	10	10	10	10	10	10
Sodium mg/ℓ	18	18	18	18	18	18
Iron mg/ℓ	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05
Active SiO_2 mg/ℓ	2,0	1,3	2,3	2,2	2,1	2,0
Total SiO_2 mg/ℓ	3,4	3,4	3,4	3,4	3,4	3,4
Nitrite mg/ℓ N	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10
Nitrate mg/ℓ	0,11	0,38	<0,10	<0,10	<0,10	<0,11
Sulphate mg/ℓ	13	15	11	13	13	13
Chloride mg/ℓ	11	<10	<10	11	11	11

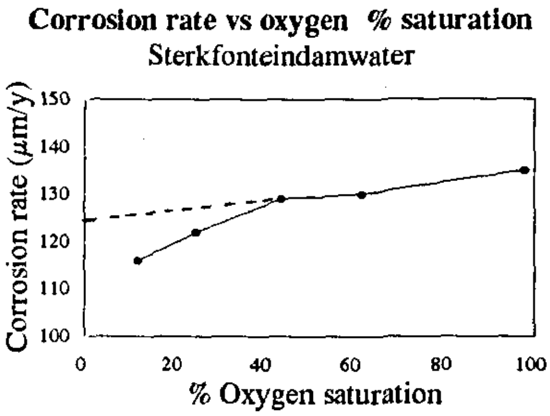


FIGURE 3.29: THE EFFECT OF OXYGEN CONCENTRATION ON THE CORROSION RATE OF MILD STEEL.

If one assumes that equation (17) is the most applicable, because it was derived from the investigation on Sterkfontein Dam water, then for 95% oxygen saturation, it will become

$$CR = 1{,}12\ (95) + 124$$

$$\approx 135\ \mu m/y$$

For any other % oxygen content the corrosion equation (F6), Appendix F, can then be multiplied by

$F(6) = CRm = [4{,}09\ Cl^- + 4{,}0\ SO_4^{2-} + 2{,}79\ Cl_2 + 9{,}78\ NO_3\text{-}N + 3{,}12\ \{T_{alk} - CCPP/F_1\} + 9{,}98\ pH - 118] \times F_1 \times F_2$.

$(F6) \times [(0{,}12\ (\%O_2) + 124)/135]$

$= (F6) \times [8{,}9 \times 10^{-4}\ (\%O_2) + 0{,}92]$ .... (a)

It now follows that if the oxygen content of the water investigated is 95%, as is the case in this investigation, the oxygen factor [ ] in equation (a) will become approximately one. For oxygen concentrations higher or lower than 95% the oxygen factor will, accordingly, become larger or smaller than one.

3.5.5 Effect of temperature on the corrosiveness of Sterkfontein Dam water at pH 7,2

The corrosion rate and conductivity of Sterkfontein Dam water was determined at various temperatures i.e. 20°C, 25°C, 30°C, 35°C, 40°C, 45°C and 50°C. Results are given in Table 3.8.

The conductivity and corrosion rate of the samples increased linearly with an increase in temperature. These relationships are presented by the linear equations.

$\text{Cond} = 1{,}5 \times 10^{-2}\,(t) + 6{,}9$ . . . . (18)

(regression coefficient r= 0,99).

and

$\text{CR} = 2{,}6\,(t) + 58{,}4$ . . . . (19)

(regression coefficient r= 0,99).

where t is temperature in °C

The relationship between the conductivity and the corrosiveness of the samples was directly proportional.

Because most of the corrosion investigations were done at 22°C equation (19) becomes

$$\begin{aligned} \text{CR} &= 2{,}6\,(22) + 58{,}4 \\ &\approx 155{,}6\ \mu\text{m/y} \end{aligned}$$

For any other temperature in °C the corrosion equation (F6) can then be multiplied by

$(F6) \times [(2{,}6\,(t) + 58{,}2)/115{,}6]$

$= (F6) \times [2{,}25 \times 10^{-2}\,(t) + 0{,}503]$ . . . . (b)

It now follows that if the temperature of the water investigated is 22°C, as was the case in this investigation, the temperature factor, [ ], in equation (b) will become approximately one. For temperatures higher or lower than 22°C the temperature factor will, respectively, become larger or smaller than one.

TABLE 3.8 CONDUCTIVITY AND CORROSION RATE VERSUS TEMPERATURE IN DEGREES CELSIUS FOR STERKFONTEIN DAM WATER

Temp. °C	20	25	30	35	40	45	50
mS/m	7,25	7,30	7,40	7,45	7,5	7,6	7,7
μm/y	114	121	138	147	162	168	196

3.5.6 Effect of polyelectrolyte flocculants on the corrosiveness of deionized water, Sterkfontein Dam water and Vaal Dam water

A 1% flocculant standard was prepared by dissolving 1g Superfloc 577 in 100 g deionized water. From this standard samples were prepared in deionized, Sterkfontein Dam and Vaal Dam water containing respectively 0,2; 0,4; 0,5; 0,8 and 1,0 mg floc/ℓ. The analysis of Sterkfontein Dam water are shown in table 3.6 and that of Vaal Dam water in Table 3.7.

No Tafel plots could be obtained for the deionized water samples, therefore 10 mg/ℓ sodium chloride was added to each sample so as to increase the conductivity somewhat.

To simulate plant conditions and the effect of the coagulant, flocculant was added to the water samples and stirred, following the normal jar test stirring method. After flocculation, the samples were filtered and the conductivity and corrosion rates determined.

In deionized water and Sterkfontein Dam water which contained no or little suspended matter no flocculation was observed while flocs did form in the turbid Vaal Dam water. In the deionized water, the conductivity increased with increasing flocculant addition, while the conductivity decreased in the Sterkfontein Dam water. The conductivity of the Vaal Dam water was approximately the same for all the samples.

The observations can be explained as follows. In deionized water with no suspended matter the increasing flocculant concentration increased the conductivity of the water and therefore the corrosiveness increased. In Sterkfontein Dam water, the flocculant probable reacted chemically with some compound in the water, whereby it lost its ionization status. Contrary to the expectations the conductivity decreased at higher flocculant dosages.

In the Vaal Dam samples, the flocculant is removed from the solution as it is trapped in flocs forming and consequently the flocculant will have no or little influence on the conductivity.

Important to note is that the corrosion rates follow the same patterns as the conductivity measurements observed with inorganic compounds.

As the conductivity of water is not increased by the addition of organic flocculants, the effect on corrosion is thought to be minimal and therefore not incorporated in the corrosion equation.

4. RESULTS FROM CONTINUOUS FLOWING MODEL SYSTEMS

The description of experiments and results to follow were done in either one of two systems which will be referred to as either the "Six Pipe" or "Two Pipe" system. Water of different chemical composition were continuously recycled through the different systems while the experiments were in progress. Chemical analysis of the water to detect any changes, and corrosion measurements using coupons or electrodes, were done during the course of the experiments. For experiments done on the "Six Pipe" system, neat Sterkfontein Dam water recycled through the first pipe of the system provided a basis for comparative observations. Conditions in the other five pipes could be varied to achieve the desired results.

The "Two Pipe" system was used in experiments where the effect of a single determinant at different levels, e.g. concentration of a chemical compound or flow rate, were studied.

REMARKS: Three facts must be emphasised. Firstly it was observed that for most of the investigations a initial decrease in alkalinity, calcium and conductivity occurred over time, whereafter it levelled off to a constant value, probably because calcium carbonate scale formation occurred and the $CaCO_3$ equilibrium was reached. This tendency will therefore not be discussed in full detail for every investigation. Secondly, the numerical values of the measured corrosion rates done under similar conditions were not always equal to that obtained with the different measuring techniques and the calculated values. It was therefore decided to rather compare observed tendencies instead of corrosion rate values as such. Thirdly, where the corrater, Calo.RE and PVC.Carb.RE gave the same tendencies only the tendency for one or two systems are shown graphically.

4.1 THE SIX PIPE SYSTEM

4.1.1 Effect of Alkalinity

a) Dosage of $CaCO_3$ (alkalinity) for negative and positive CCPP'S.

The alkalinity of Sterkfontein Dam water was determined as 35 mg/ℓ $CaCO_3$ and used as the control in the first pipe. In the other five pipes the alkalinity was adapted with calcium bicarbonate (See 2.4) solution to respectively 70, 81, 81, 88 and 94 mg/ℓ for the second to sixth pipe after the pH values were adjusted to about 8,2. The CCPP values as calculated with the Stasoft and JTG programs were: - 8,0; - 0,7; + 2,98; + 2,22; + 2,41; + 2,13 for pipes No 1 to No 6 respectively.

b) Measurements and calculations

Coupon, corrater and ECI corrosion rate measurements were taken on seven consecutive days and then again on the tenth day from the beginning of the experiment. From these analyses the corrosion indexes and corrosion rates were calculated with the computer programmes developed by the Rand Water. The CCPP's were calculated with the JTG and Stasoft programs.

c) Results

Results of alkalinity, corrosion rates and calculated indices versus time and CCPP are shown in Figures 4.1 to 4.13.

Analyses showed that the alkalinity, Figure 4.1 increased with increasing dosage of calcium bicarbonate. At the same time CCPP values became less negative. A drop in alkalinity was noticed with increasing positive CCPP values. The same tendencies were observed for calcium content, total carbonate specie concentration (C_t) and conductivity. The reduction in alkalinity at increasing CCPP probably indicated $CaCO_3$ precipitation. Corrosion rate measurements for the coupons and Calo.RE (Figures 4.2 and 4.3), which compared favourably with the tendencies for the calculated corrosion rates bases on Rand Water equation (Figures 4.4 and 4.5) follow the same tendencies as those obtained for the water analysis. Results obtained with the corrater and PVC.Carb.RE showed the same tendencies as for the corrosion of coupons shown in Figure 4.2 and 4.3. For increasing CCPP values from - 9 to zero the conductivity of the water increased, because of calcium bicarbonate dosage and $CaCO_3$ staying in solution, while for CCPP values > 0 the conductivity decreased probably because of $CaCO_3$ precipitation. Except for the scattered results obtained for the corrosion rate of coupons at CCPP values < 0 the tendencies for the corrosion rates measured by other means are the same as for those obtained for the chemical analysis and conductivity.

Analyses by means of X-ray diffraction and fluorescence of corrosion products showed a definite decrease in iron to calcium ratios from high negative CCPP values to the positive CCPP values (table 4.1). All the corrosion products formed at the positive CCPP values showed high calcium content while the corrosion products formed at water with negative CCPP values had a relative low calcium content.

TABLE 4.1 IRON TO CALCIUM RATIO'S FOR INCREASING CCPP FROM HIGH NEGATIVE TO HIGH POSITIVE VALUES

CCPP in mg/ℓ $CaCO_3$	-5,7	-0,94	+1,7	+1,7	+1,7	+2,0
Fe:Ca ratio	5,9:1	2,7:1	1,7:1	1,0:1	2,3:1	1,9:1

Values calculated for different indices were plotted as function of CCPP values (Figure 4.6 to 4.13), from the results obtained its follows that:

a. Langelier Saturation Index (LSI)
Values greater than -0,5 indicated water that was non-corrosive and from Figure 4.6 it can be seen that these values coincided with all positive CCPP values.

b. Ryznar Stability Index (RSI)
Values greater than 7,0 indicate corrosive water but in Figure 4.7 it can be seen that most of these waters, which the index predicted as being corrosive or non-scale forming, had positive CCPP values that can be as high as 19,4 if the line is extrapolated to a index value of 7,0. This discrepancy may be because the Ryznar Stability Index was mainly developed for boiler and cooling tower waters at high temperature. The results depicted in Figure 4.7 indicated that a value of >9,0 instead of >7,0 could be more realistic for potable water.

c. Larson Index (LI)
The Larson Index incorporates the effect of chloride and sulphate on the corrosion process in the equation and predicts corrosive water.

$([Cl^-] + [SO_4^{2-}]):Alk < 0{,}2$ or $Alk:([Cl^-] + [SO_4^{2-}]) > 5{,}0$

According to experiments water with CCPP value > 2,5 was not corrosive (See Figure 4.8).

d. Driving force Index (DFI)
Calculated values >1,0 indicates non-corrosive water which coincides with non-corrosiveness at CCPP values >1,0 as can be seen in Figure 4.9.

e. Riddick Corrosion Index (RCI)
Calculated values between 5 and 25 indicate non-corrosive water which corresponds with all negative CCPP values from zero to - 6,69. For values <5 it indicates scale forming and corresponds to all positive CCPP values as can be seen in Figure 4.10.

f. Casil Index (CI)
Calculated values >0,1 indicated non-corrosive water but none of the calculated values showed any correlation with the other results as shown in Figure 4.11.

g. Aggressive Index (AI)
Calculated values for the Aggressive Index indicate non-corrosive water for values >12 which is in agreement with CCPP values >2 (Figure 4.12).

h. Feigenbaum, Gal-or, Yahalom (Y)
Calculated values for this index (Figure 4.13) indicate moderate corrosive water for values between 200 and 500 which relates to CCPP values of between 1,0 and 4,5 as mg/ℓ $CaCO_3$. Mild corrosion can be expected at index values > 500 which corresponds to CCPP values of > 4,5 as mg/ℓ $CaCO_3$.

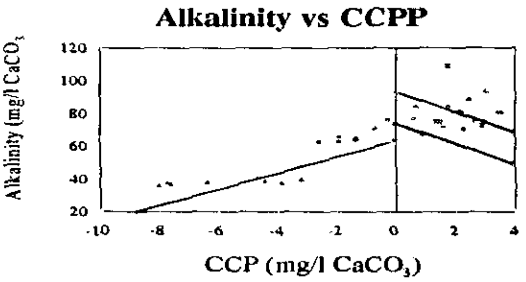


FIGURE 4.1: ALKALINITY VERSUS INCREASING CCPP

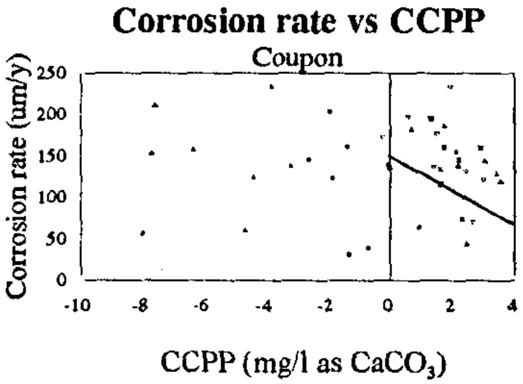


FIGURE 4.2: CORROSION RATES MEASURED WITH COUPONS VERSUS CCPP

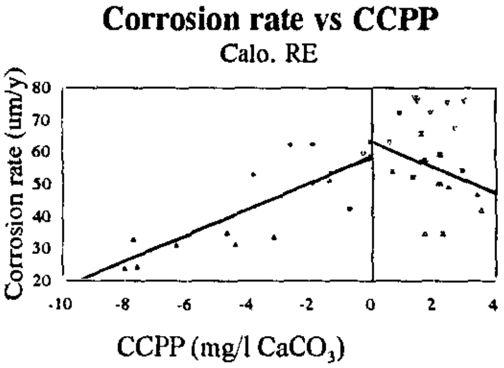


FIGURE 4.3: CORROSION RATES MEASURED ON THE CALO.RE VERSUS CCPP

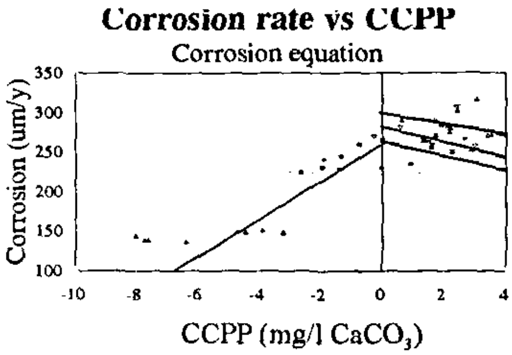

Corrosion rate vs CCPP
Corrosion equation

FIGURE 4.4

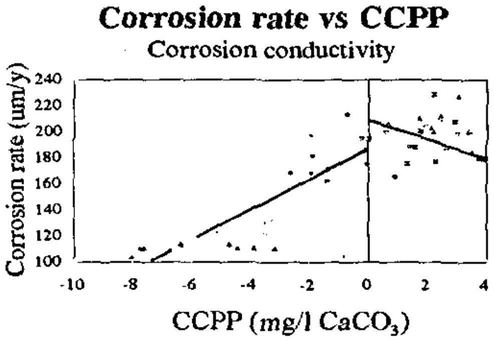

Corrosion rate vs CCPP
Corrosion conductivity

FIGURE 4.5

FIGURE 4.4 AND 4.5: CALCULATED CORROSION RATES BASED ON RAND WATER CORROSION EQUATION VERSUS CCPP

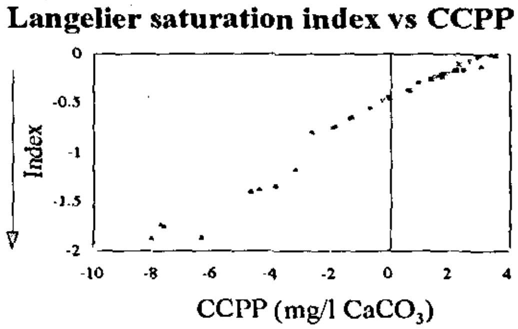

Langelier saturation index vs CCPP

FIGURE 4.6: CALCULATED VALUES FOR DIFFERENT CORROSION INDICES VERSUS CCPP

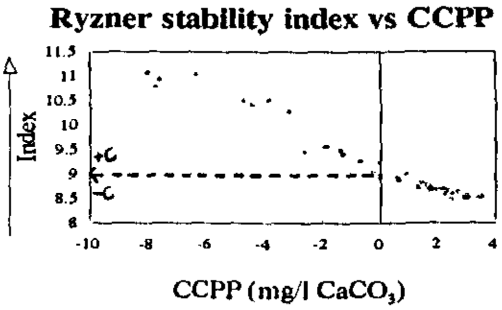


FIGURE 4.7

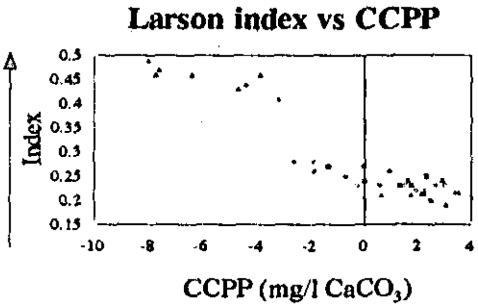


FIGURE 4.8

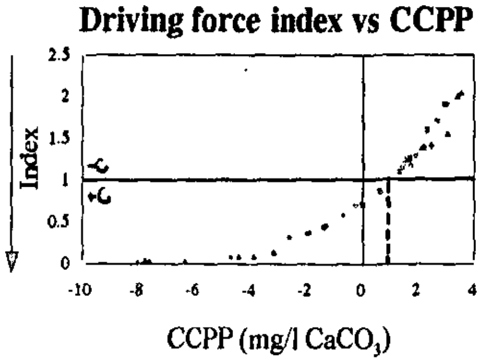
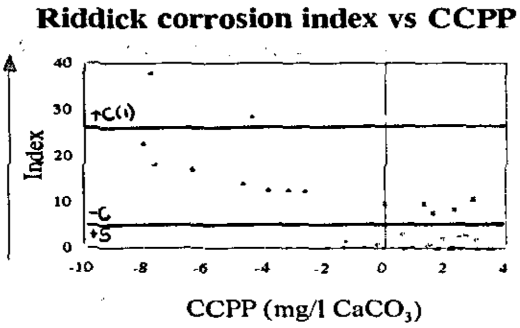
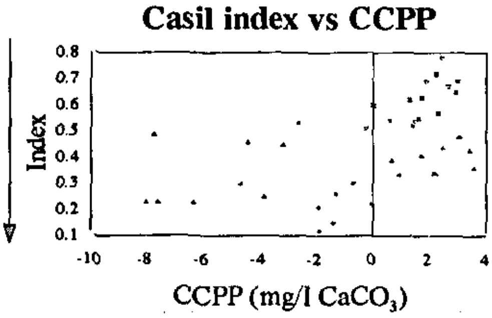


FIGURE 4.9

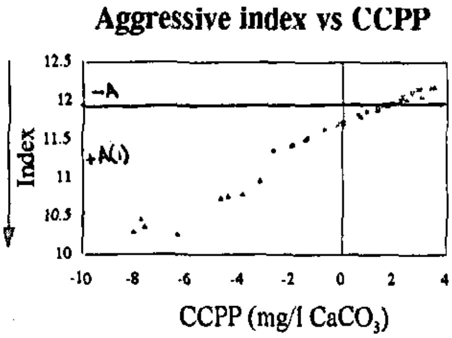
FIGURES 4.7 TO 4.9: CALCULATED VALUES FOR DIFFERENT CORROSION INDICES VERSUS CCPP



FIGURES 4.10

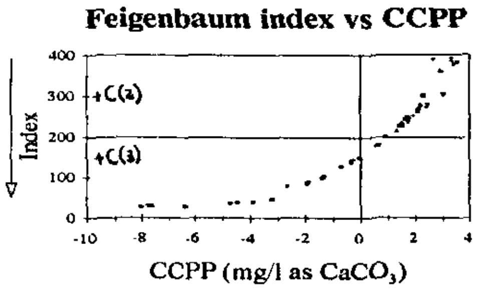


FIGURES 4.11



FIGURES 4.12

FIGURES 4.10 TO 4.12: CALCULATED VALUES FOR DIFFERENT INDICES VERSUS CCPP


Feigenbaum index vs CCPP

Legends used for graphs in Figures 4.1 to 4.13

□	Alkalinity 36 in mg $CaCO_3/\ell$
+	Alkalinity 70 in mg $CaCO_3/\ell$
△	Alkalinity 81 in mg $CaCO_3/\ell$
▾	Alkalinity 81 in mg $CaCO_3/\ell$
x	Alkalinity 88 in mg $CaCO_3/\ell$
♦	Alkalinity 94 in mg $CaCO_3/\ell$

FIGURE 4.13: CALCULATED VALUES FOR DIFFERENT INDICES VERSUS CCPP

4.1.2 The effect of silicate

Silicate ($Na_20/3,3\ SiO_2$), was dosed at 5 and 10 mg/l as SiO_2 into two of the pipes in the six pipe system.

RESULTS

Corrosion rates were determined every second day by method of the electrochemical and coupon methods, while at the same time samples were taken for chemical analysis. The corrosion rates obtained with the coupons and PVC.Carb.RE versus SiO_2 content are graphically represented in Figures 4.14 and 4.15. Only two indices, namely the CI and RCI, were investigated because they were the only indices that make provision for silicate in their equations. The calculated values for these indices are presented graphically in Figures 4.16 and 4.17. The change in SiO_2 concentration versus time is graphically represented in Figure 4.18.

The alkalinity, conductivity and SiO_2 concentrations in all the pipe systems decreased with time. Decreasing alkalinity and a corresponding decrease in conductivity may be as a result of the formation of calcium carbonate deposits while the decrease in SiO_2 concentration (Figure 4.18) may be due to the incorporation of SiO_2 in the corrosion product. The graphically represented corrosion rates of coupons versus mg/ℓ SiO_2 content (Figure 4.14) also show a decrease in corrosion rates with an increase in SiO_2 concentration from 2 to about 10 mg/ℓ SiO_2. Higher corrosion rates were observed for SiO_2 concentrations greater than about 12 mg/ℓ SiO_2. The PVC.Carb.RE system, Figure 4.15, showed the same tendency as the coupons.

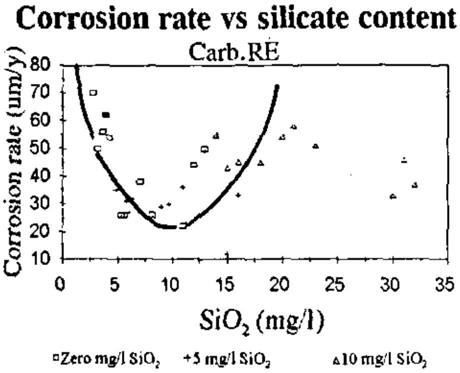


FIGURE 4.14

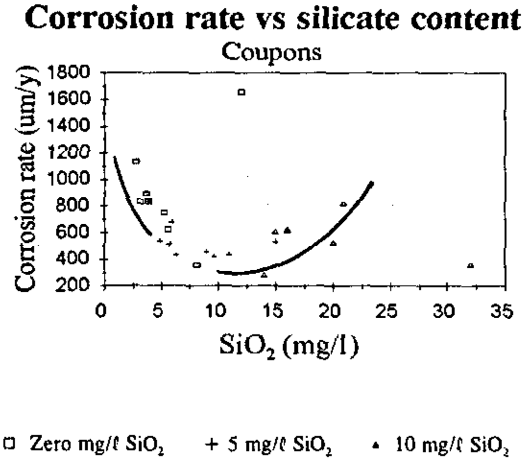


FIGURE 4.15

□ Zero mg/ℓ SiO_2
\+ 5 mg/ℓ SiO_2
♦ 10 mg/ℓ SiO_2

FIGURES 4.14 AND 4.15 MEASURED CORROSION RATES ON PVC.CARB.RE SYSTEM AND COUPONS VERSUS INCREASING SiO_2 CONTENT

The RCI Index (Figure 4.16) indicated that the water with high silicate dosage was less corrosive for the full duration of the investigation, although the CI Index (Figure 4.17) indicated that all the waters were slightly corrosive, it also indicated that the water with high silicate was less corrosive than the water with low silicate content.

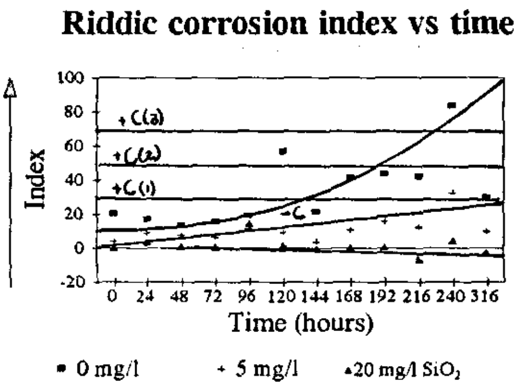


FIGURE 4.16

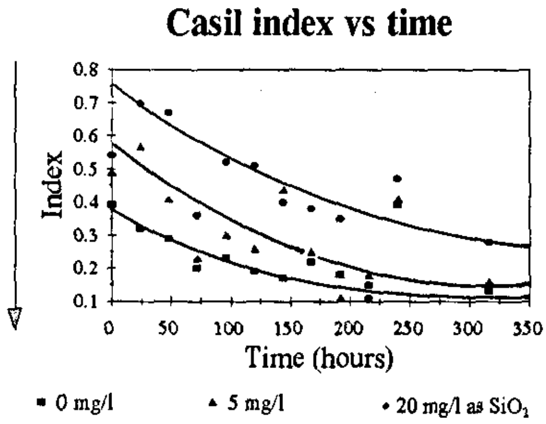


FIGURE 4.17

FIGURES 4.16 AND 4.17: CHANGE IN INDEX VALUES VERSUS TIME IN THE STUDY OF THE EFFECT OF SILICA ON CORROSION

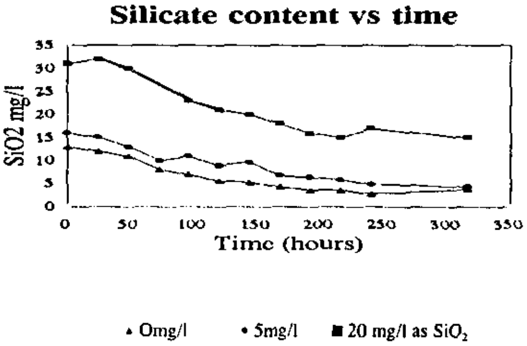


FIGURE 4.18: CHANGE IN SILICA CONCENTRATION VERSUS TIME IN THE STUDY OF THE EFFECT OF SILICA ON CORROSION

4.1.3 Effect of organic coagulants

Organic coagulant dosages were zero for the first two pipes, 4 mg/ℓ for the third and 10 mg/ℓ for the fourth pipe.

RESULTS

Corrosion rate measurements and samples were taken 24 hours after commencing the experiment and thereafter at two days intervals.

The results obtained indicated higher corrosion rates for water dosed with organic coagulant than without organic coagulant with tendencies the same as those obtained for alkalinity and conductivity.

4.1.4 Effect of chlorine

Chlorine dosages were respectively zero, 1, 5 and 10 mg/ℓ. The chlorine concentration was determined immediately after chlorine dosages and repeated thereafter on a daily basis. Corrosion rate measurements were taken twenty four hours after commencement of the investigation and daily thereafter.

Tendencies for alkalinity and pH changes versus time are shown in Figures 4.19 and 4.20. Corrosion rate measurements for the coupons are shown in Figure 4.21, and for the corrater in Figure 4.22.

RESULTS

Chlorine concentration in pipe systems three, four and five, directly after dosage were 1,0; 4,9 and 9,8 mg/ℓ as $C\ell_2$, but after 24 hours no free chlorine could be detected. Conductivity, alkalinity and calcium decreased substantially with time during the first 40 to 60 hours in the water except for in the first pipe in which the neat Sterkfontein Dam water was used. The corrosion rates measured with the coupons decreased after 24 hours in water containing chlorine, while corrosion rates measured with the corrater increased. Corrosion rates measured with the coupons increased after 100 hours exposure time with lowest corrosion rates measured in water containing the highest chlorine concentration. Corrosion rates measured with the corrater was the lowest in water with 1 and 5 mg/ℓ Cl_2 after 100 hours exposure time, but the highest corrosion rates were obtained at 10 mg/ℓ chlorine. The pH decreased during the first 70 hours whereafter the decrease was not so drastic and even increased slightly in some cases. The pH of water containing 5 and 10 mg/ℓ of chlorine was lower than the pH of Sterkfontein Dam water without and with 1 mg/ℓ chlorine in which the alkalinity had been adjusted.

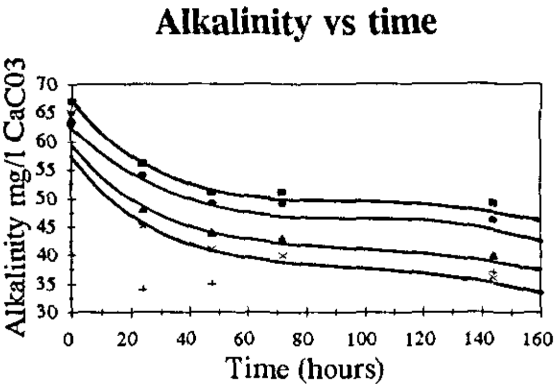


FIGURE 4.19: CHANGE IN ALKALINITY WITH TIME IN THE STUDY OF THE EFFECT OF CHLORINE ON THE CORROSION RATE OF MILD STEEL

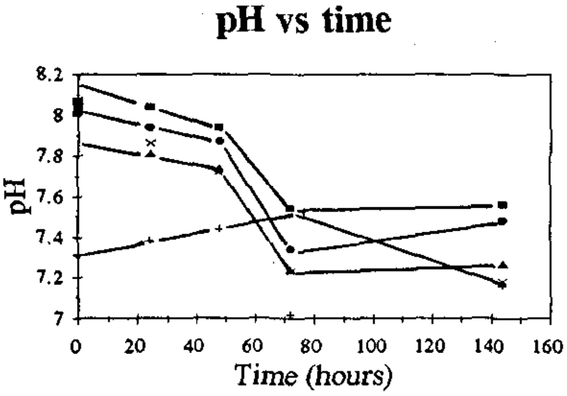


FIGURE 4.20: CHANGE IN pH WITH TIME IN THE STUDY OF THE EFFECT OF CHLORINE ON THE CORROSION RATE OF MILD STEEL

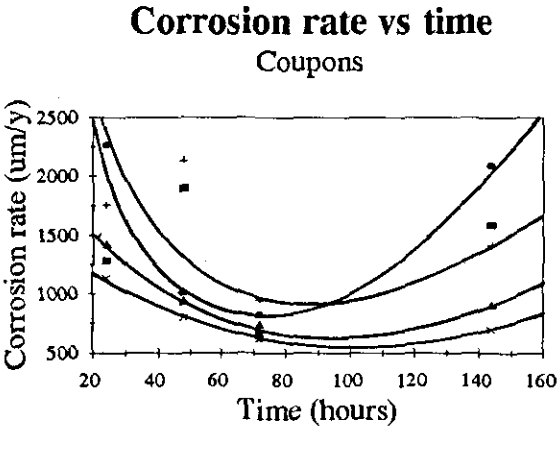
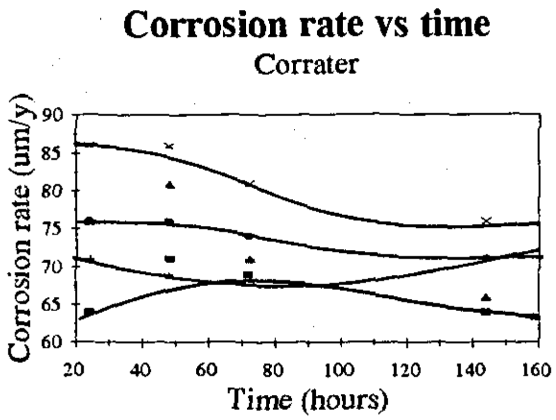


FIGURE 4.21: CORROSION RATE MEASURED WITH COUPONS IN THE STUDY OF THE EFFECT OF CHLORINE ON THE CORROSION RATE OF MILD STEEL



+	Neat Sterkfontein Dam water
o	0 mg/ℓ chlorine
■	1 mg/ℓ chlorine
△	5 mg/ℓ chlorine
x	10 mg/ℓ chlorine

FIGURE 4.22: **CORROSION RATE MEASURED WITH THE CORRATER IN THE STUDY OF THE EFFECT OF CHLORINE ON THE CORROSION RATE OF MILD STEEL**

4.1.5 Effect of monochloramine

The alkalinity of the water in four of the pipe systems were adjusted to 80 mg/ℓ as calcium carbonate at pH 8,2 while the first system was filled with neat Sterkfontein Dam water as a control. Monochloramine was dosed at respectively 1, 5 and 10 mg/ℓ into systems 3, 4 and 5.

Monochloramine was prepared by bubbling chlorine gas through chilled water whereafter sodium hydroxide was added till a pH of 9 was obtained. The chlorine content was then determined and ammonium sulphate added so as to obtain a chlorine to nitrogen ratio of 1:4. The monochloramine content of the latter solution was determined and the volume required for 1, 5 and 10 mg/ℓ dosages calculated.

RESULTS

Samples for chemical analysis were taken on five consecutive days and the results for specific analyses are shown in Table 4.2. Changes in corrosion rates of coupons are shown in Figure 4.23 and the corrosion rates measured by the corrater in Figure 4.24. Changes in alkalinity versus time are shown in Figure 4.25.

Alkalinity, calcium and conductivity concentrations decreased with time (Table 4.2) suggesting the precipitation of calcium carbonate. The corrosion rates in water containing monochloramine were compared to that in neat Sterkfontein Dam water and water in which the alkalinity had been adjusted but contained no combined chlorine. During the first 50 hours the corrosion rates of coupons in water containing 1 and 5 mg/ℓ NH_2Cl were lower than the water without NH_2Cl. The corrosion rate in water with 10 mg/ℓ was the highest of the three. After 50 hours the corrosion rate in the water containing 1 mg/ℓ NH_2Cl was still less than the Sterkfontein Dam water with adjusted alkalinity.

Corrosion measured on the corrater was the lowest in water containing 1 mg/ℓ NH_2Cl.

After 50 hours the highest corrosion in all systems with both the coupons and the corrater was measured in the system with 10 mg/ℓ monochloramine. No monochloramine could be detected in the system after 50 hours.

TABLE 4.2 SPECIFIC CHEMICAL ANALYSIS OF WATER SAMPLES IN WHICH THE CORROSION EFFECT OF MONOCHLORAMINE WAS EXAMINED.

a) Change in alkalinity against time

Time: hours	Pipe Number				
	1	2	3	4	5
	Sterkfontein	80 mg/ℓ Alkalinity	80 mg/ℓ Alkalinity + 1 mg/ℓ NH_2Cl	80 mg/ℓ Alkalinity + 5 mg/ℓ NH_2Cl	80 mg/ℓ Alkalinity + 10 mg/ℓ NH_2Cl
24	33	51	66	63	67
48	33	49	63	60	62
72	34	47	58	57	58
120	33	46	54	52	56
144	34	53	47	51	54
mean	(33)	(49)	(58)	(57)	(59)

b) Change in calcium concentration against time

Time: hours	Pipe Number				
	1	2	3	4	5
	Sterkfontein	80 mg/ℓ Alkalinity	80 mg/ℓ Alkalinity + 1 mg/ℓ NH_2Cl	80 mg/ℓ Alkalinity + 5 mg/ℓ NH_2Cl	80 mg/ℓ Alkalinity + 10 mg/ℓ NH_2Cl
24	8,3	25	21	19	16
48	8,4	23	18	17	15
72	8,4	23	18	16	13
120	8,6	23	16	14	12
144	9,4	16	14	14	11

c) Change in conductivity against time

Time: hours	Pipe Number				
	1	2	3	4	5
	Sterkfontein	80 mg/ℓ Alkalinity	80 mg/ℓ Alkalinity + 1 mg/ℓ NH_2Cl	80 mg/ℓ Alkalinity + 5 mg/ℓ NH_2Cl	80 mg/ℓ Alkalinity + 10 mg/ℓ NH_2Cl
24	10	19	16	10	21
48	10	19	16	18	20
72	10	19	15	18	20
120	10	18	14	17	19
144	10	14	19	17	19
mean	(10)	(18)	(16)	(18)	(20)

TABLE 4.3 CHANGE IN MONOCHLORAMINE CONCENTRATION WITH TIME IN PIPE NUMBERS 3, 4 AND 5

Time: Hours	NH_2Cl in mg/ℓ		
0	1,1	5,5	11,0
24	0,6	1,1	0,0
48	0,1	0,2	0,0
72	0,0	0,0	0,0

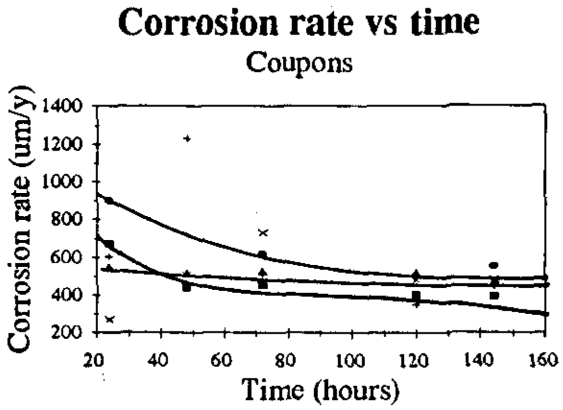


FIGURE 4.23

FIGURE 4.23: THE EFFECT OF MONOCHLORAMINE ON THE CORROSION RATE OF MILD STEEL

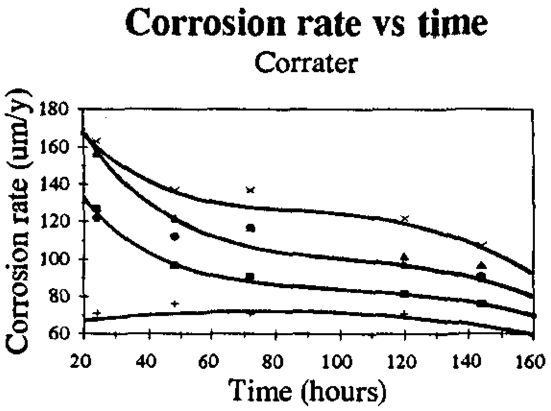


FIGURE 4.24

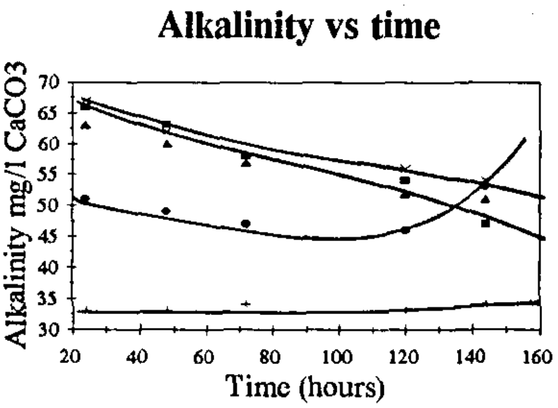


FIGURE 4.25

FIGURE 4.24 AND 4.25: THE EFFECT OF MONOCHLORAMINE ON THE CORROSION RATE OF MILD STEEL

+	Neat Sterkfontein Dam water
o	0 mg/ℓ Monochloramine
■	1 mg/ℓ Monochloramine
△	5 mg/ℓ Monochloramine
x	10 mg/ℓ Monochloramine

4.2 THE TWO PIPE SYSTEM

4.2.1 The effect of chloride

In the laboratory investigation it was found that a linear relation exists between the chloride concentration and the corrosion rate of mild steel. It was also found that a linear relation exists between the corrosion rate and the conductivity which increased relative to the chloride concentration. To determine whether the chloride ion or the conductivity causes an increase in corrosion rate, samples with the same conductivity but increasing chloride concentration were investigated.

To confirm the results obtained in the laboratory investigation, the corrosiveness of water with high and low chloride concentrations were investigated in the two pipe system. Water in the first pipe was dosed with chloride to a level of 30 mg/ℓ and in the second pipe to a level of 5 mg/ℓ as Cl^-. Four sets of samples for chemical analysis and four sets of corrosion rate measurements were taken over a period of 288 hours.

RESULTS

Tendencies for the corrosion rates of coupons are shown in Figure 4.26. Figures 4.27 and 4.28 show the corrosion rates for respectively the Calo.RE system, and Rand Water Corrosion equation. Tendencies for the indices are shown in Figures 4.29 to 4.32 for respectively the Riddick Corrosion Index, Larson Index, Casil Index and Feigenbaum Index.

Alkalinity and conductivity, decreased with time. Corrosion rates measured with the coupons and Calo.RE systems as well as the calculated corrosion rates, showed the same tendencies as those for the conductivity. The corrosion rates at the high chloride concentrations were higher than the corrosion rates at the low chloride concentration. Tendencies for the Casil, Larson and Riddick corrosion indices correlate with the results obtained for the corrosion rate measurements. The Feigenbaum Index indicated an initial increase in corrosivity during the first twenty hours with the corrosivity at the high chloride concentration the highest. It was also observed that after 140 hours exposure time the pH increased more rapidly to values above 7,5 as was the case for water with low chloride dosed. This latter observation could lead to the chemical formation of turbercule.

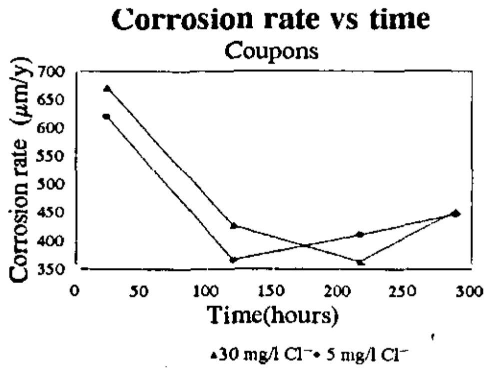


FIGURE 4.26

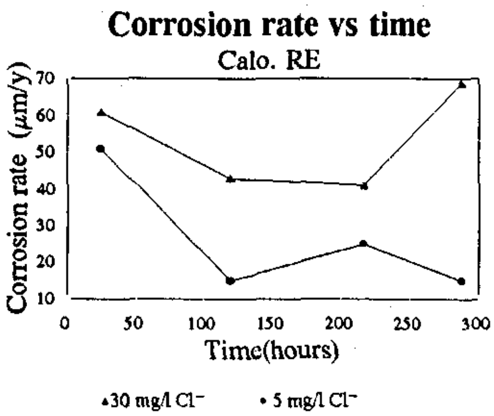


FIGURE 4.27

FIGURES 4.26 AND 4.27 THE EFFECT OF CHLORIDE ON THE MEASURED CORROSION RATE OF MILD STEEL

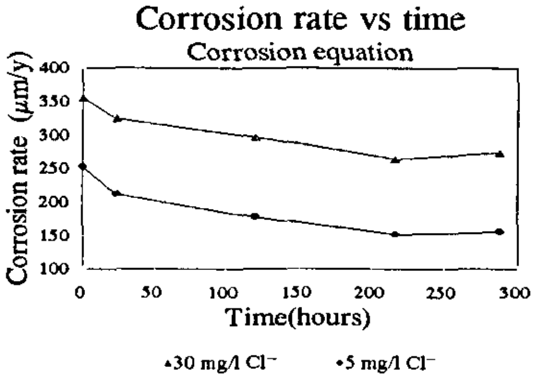


FIGURE 4.28: THE EFFECT OF CHLORIDE ON THE CALCULATED CORROSION RATE OF MILD STEEL

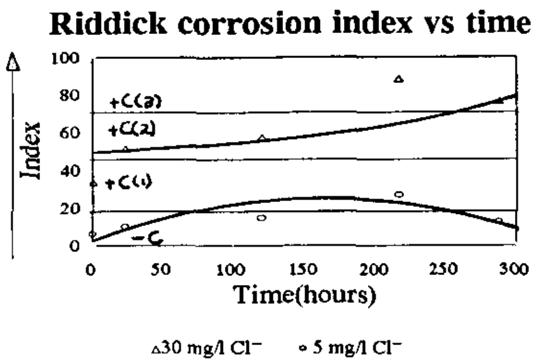


FIGURE 4.29: CALCULATED INDEX VALUES INDICATING THE EFFECT OF CHLORIDE ON THE CORROSION RATE OF MILD STEEL

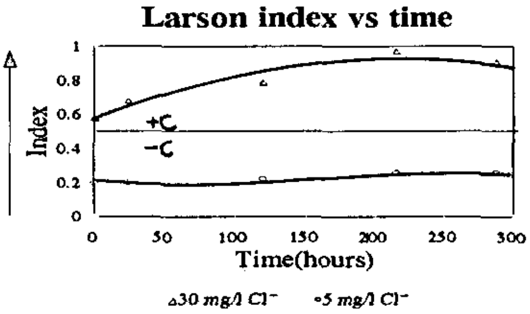


FIGURE 4.30

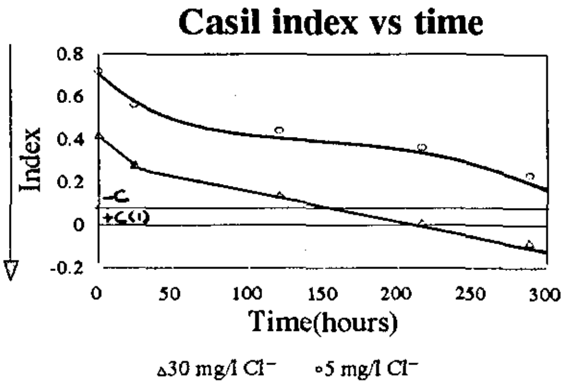


FIGURE 4.31

FIGURES 4.30 AND 4.31: CALCULATED INDICES VALUES INDICATING THE EFFECT OF CHLORIDE ON THE CORROSION RATE OF MILD STEEL

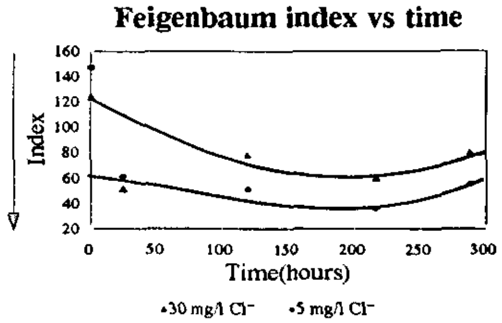


FIGURE 4.32 **CALCULATED INDICES VALUES INDICATING THE EFFECT OF CHLORIDE ON THE CORROSION RATE OF MILD STEEL**

4.2.2 The effect of sulphate

The chemical adjustment of Sterkfontein Dam water for this experiment was identical to that in which the effect of chloride was investigated. Sulphate concentration were respectively 5 mg/ℓ and 30 mg/ℓ. Readings and analysis were obtained 24 hours after commencing the investigation and then every seven days thereafter for seventeen days.

RESULTS

Changes in conductivity versus time are shown in Figure 4.33. Corrosion rates obtained with the coupons and the Calo.RE system are presented in Figures 4.34 and 4.35. Results for the Larson Index value are shown in Figure 4.36.

The alkalinity and conductivity decreased with time with a trend towards a constant value. The same tendencies were observed for the corrosion rates measured with the coupons and Calo.RE system.

The conductivity and corrosion rates were consistently higher for a higher sulphate concentration. This may be due to the higher alkalinity in the water with high sulphate dosage. The values for the LI and CI indicated higher corrosivity in the water with high sulphate dosage compared to the water with low sulphate dosage. The Feigenbaum, Gal-or, Yahalom Index (Y), however, indicates the opposite.

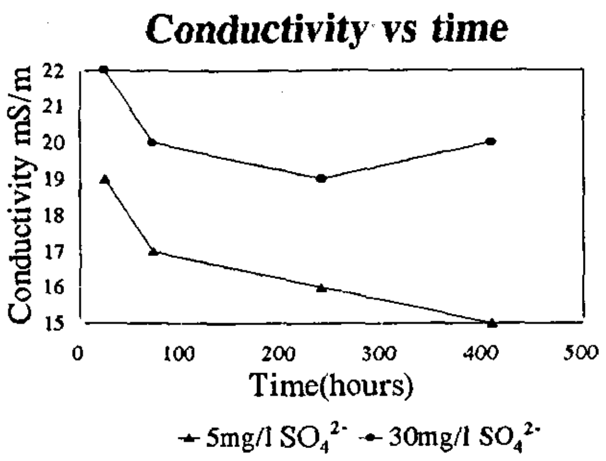


FIGURE 4.33

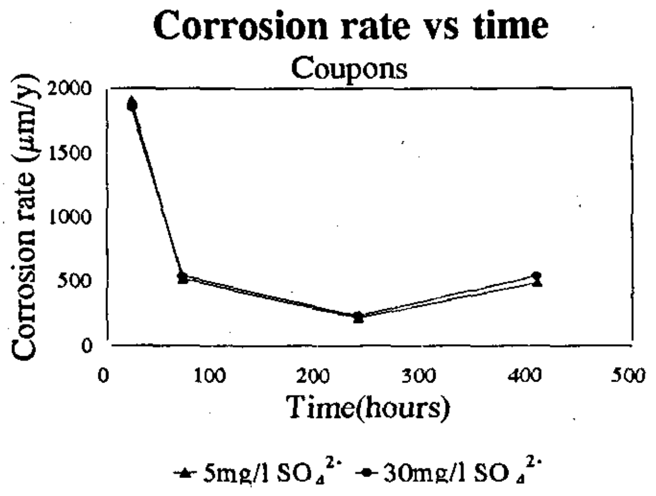


FIGURE 4.34

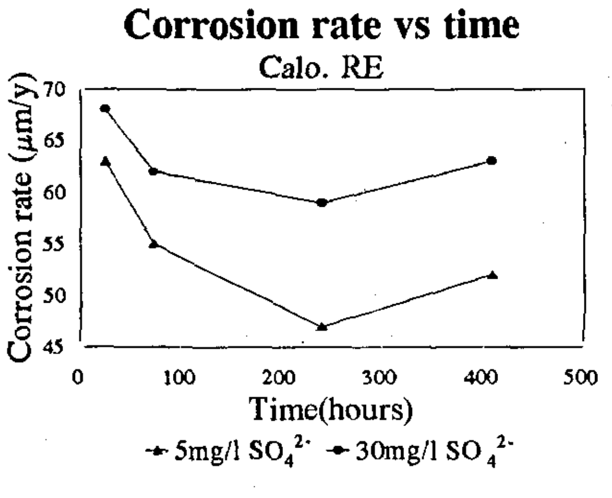


FIGURE 4.35

FIGURES 4.33 TO 4.35 CHANGES IN CONDUCTIVITY, CORROSION RATE MEASURED WITH COUPONS AND ELECTRODES AGAINST TIME IN THE STUDY OF DIFFERENT SULPHATE CONCENTRATIONS

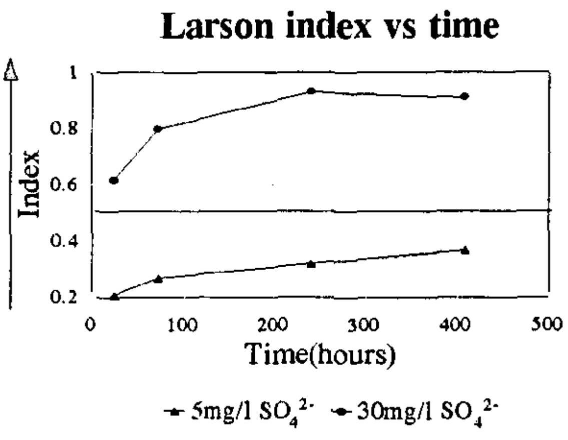


FIGURE 4.36: CHANGE IN THE LARSON INDEX VERSUS TIME IN THE STUDY OF DIFFERENT SULPHATE CONCENTRATIONS

4.2.3 The effect of silicate

a) High and Low Silicate Dosage

Silicates has potential, and is being used, to prevent corrosion in water distribution systems. For this reason it was included in the study.

To investigate the effect of silicate, 5 mg/ℓ as SiO_2 was dosed into one pipe system and 50 mg/ℓ as SiO_2 was dosed into the other to represent low and high dosages. The first corrosion rate readings and water samples for chemical analysis were taken 24 hours after the experiment commenced and were then repeated with seven day intervals.

RESULTS

Tendencies for alkalinity are graphically represented in Figure 4.37. Measured corrosion are represented in Figure 4.38, for the corrater and in Figure 4.39 for the coupons. From Figure 4.37 it can be seen that the alkalinity decreased in time. The alkalinity and conductivity of water with high silicate dosage (50 mg/ℓ as SiO_2) was higher than that of water with low silicate dosage. Initial corrosion rates measured with the coupons were the highest in water with high silicate dosage compared to water with low SiO_2 content. After about 400 hours the corrosion rates were about the same. More or less the same tendencies were observed for the corrater readings as shown in Figure 4.38.

Corrosion rates measured with the PVC.Carb.RE and Calo.RE systems also show higher corrosion rates at the high silicate dosage compared to the low silicate dosage. Corrosion products of the coupons from the two pipes were collected separately and treated with Hibitex, whereafter the Hibitex was analysed for calcium, iron and SiO_2 content. The chemical analysis indicated that the corrosion products in the water with high silicate dosage contained about 30% more silicate as SiO_2 (Table 4.4) than the corrosion product formed in the water with low silicate dosage.

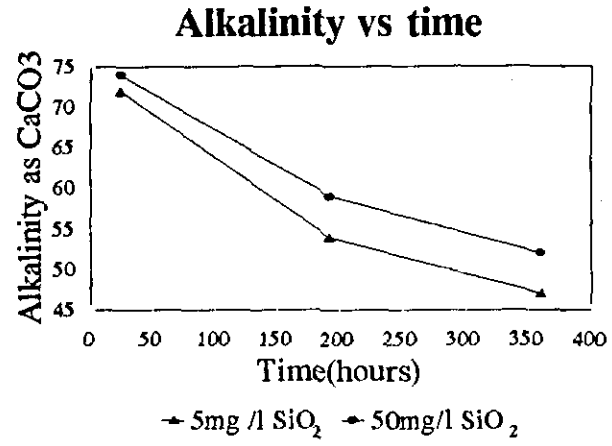


FIGURE 4.37: CHANGES IN ALKALINITY AND THE EFFECT OF SILICA ON THE CORROSION OF MILD STEEL IN THE STUDY OF SILICA ON CORROSION.

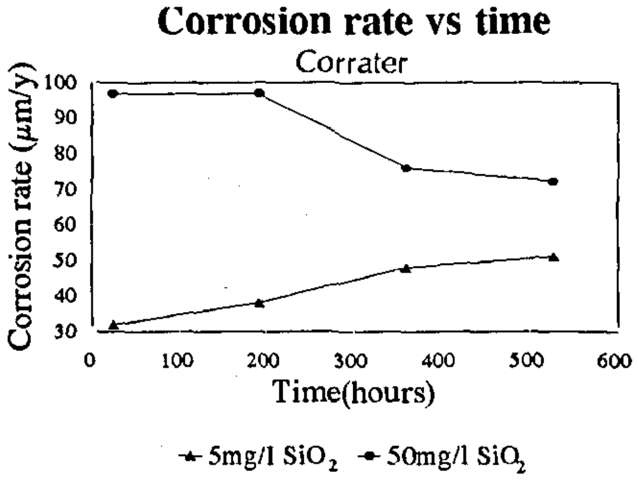


FIGURE 4.38

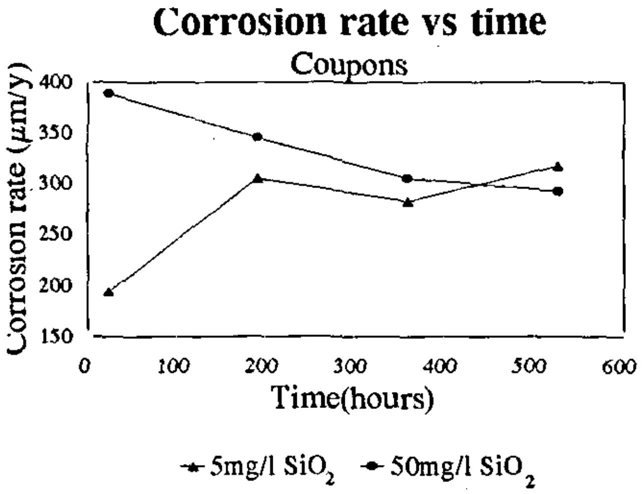


FIGURE 4.39

FIGURES 4.38 AND 4.39: CHANGES IN ALKALINITY AND THE EFFECT OF SILICA ON THE CORROSION OF MILD STEEL IN THE STUDY OF SILICA ON CORROSION.

TABLE 4.4 AVERAGE CHEMICAL ANALYSIS OF CORROSION PRODUCTS ON ALL COUPONS FORMED AS A RESULT OF SILICATE TREATMENT AT TWO CONCENTRATIONS.

%	5 mg/ℓ SiO_2	50 mg/ℓ SiO_2
Fe_2O_3	97,2	97,19
$CaCO_3$	2,64	2,64
SiO_2	0,12	0,17

b) Activated and Non-activated silica

To determine if there is a difference between the effects of activated and non-activated silica on the corrosion of mild steel two one litre solutions each containing 10 mg/ℓ SiO_2 were prepared. The pH in one of the solutions was reduced to 8 by bubbling CO_2 gas through to activate the SiO_2 while the pH of the other sample was left at 10,6. The SiO_2 concentration in both the activated and non-activated was 10 mg/ℓ.

RESULTS

Samples for chemical analysis and corrosion rate measurements were taken 24 hours after commencing the experiment and then at 7 day intervals thereafter for 22 days. The change in conductivity and effect of silica on corrosion are graphically represented in Figure 4.40. Corrosion rates of the coupons are shown in Figure 4.41, and Figure 4.42 for the Calo.RE system. Calculated indices values are shown in Figure 4.43 for the RCI and Figure 4.44 for the CI. The conductivity of water with activated silica was higher than for non-activated silica but the concentration of both solutions decreased with time. Corrosion rates of coupons were about the same in both activated and non-activated silica solutions. Corrosion rates measured with the Calo.RE were higher for the activated than for the non-activated silica. All the indices, LSI, RCI and CI indicated non-corrosive water for both activated and non- activated silica. Only the CI indicate more corrosive water for the activated silica than the non-activated silica and in this respect coincided with most of the different corrosion rate measurements.

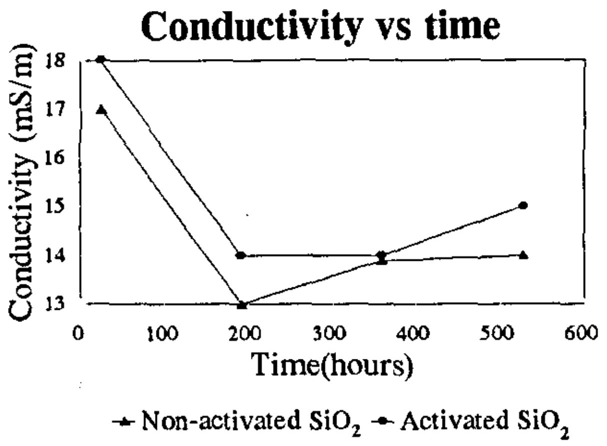


FIGURE 4.40: A CHANGE OF CONDUCTIVITY AND THE EFFECT OF NON-ACTIVATED AND ACTIVATED SILICA ON THE CORROSION OF MILD STEEL AGAINST TIME.

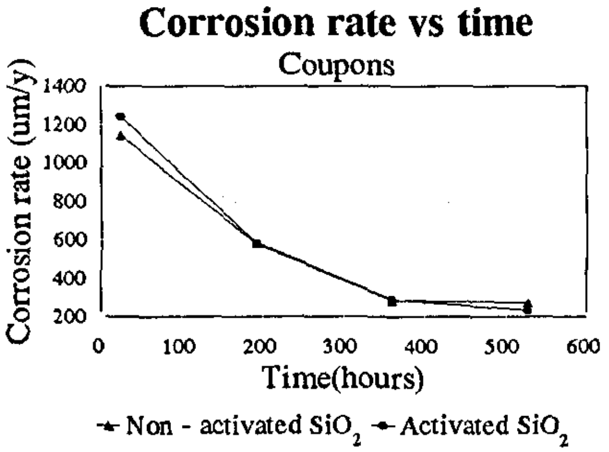


FIGURE 4.41

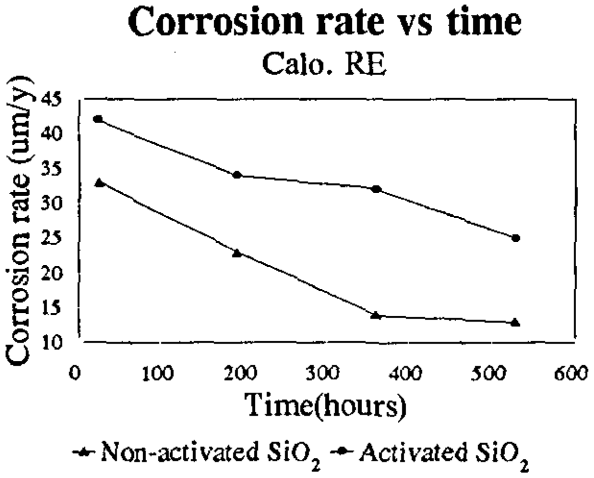


FIGURE 4.42

FIGURE 4.41 AND 4.42: CHANGE OF CONDUCTIVITY AND THE EFFECT OF NON-ACTIVATED AND ACTIVATED SILICA ON THE CORROSION RATES OF MILD STEEL AGAINST TIME.

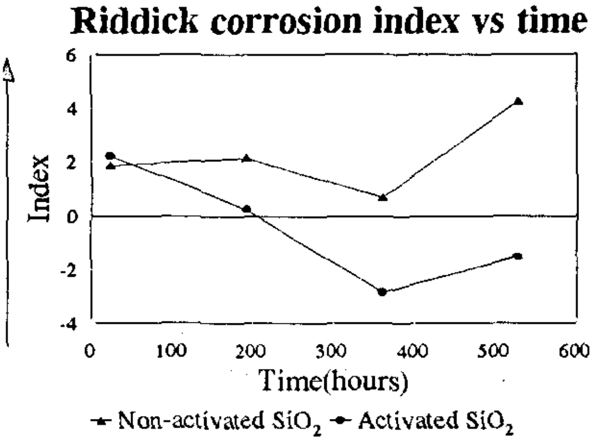


FIGURE 4.43

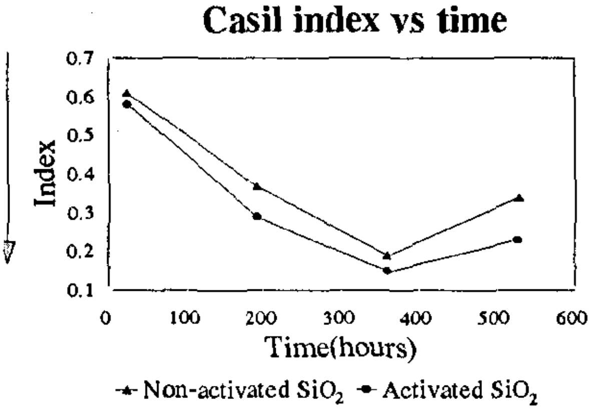


FIGURE 4.44

FIGURE 4.43 AND 4.44: CHANGES IN THE CALCULATED INDICES VALUES OF NON-ACTIVATED AND ACTIVATED SILICA SOLUTIONS AGAINST TIME.

4.2.4 Effect of oxygen

In this study the aim was to expose the coupons to water with relatively high and low dissolved oxygen concentrations. Low levels of oxygen concentration was obtained by stripping all oxygen from the water in the holding vessel by bubbling nitrogen gas through it. Afterwards the container was covered to prevent any further contact with the atmosphere. Furthermore the outlet pipe from the pipe system metering the recycled water was submerged to avoid splashing.

In the solution in which a high dissolved oxygen concentration was required the recycled water was allowed to make contact with the atmosphere where it dropped into the holding vessel.

By following this procedure the oxygen concentration could be maintained at 2,9 and 7,1 mg/ℓ which is equal to 40 and 95% saturation in the respective systems.

RESULTS

Calculated indices values are shown in Table 4.5. Measured corrosion rates for the coupons are shown in Figure 4.45.

The alkalinity, calcium content and conductivity decreased with time and levelled off at constant values after about 60 hours. The measured corrosion rates of coupons also decreased with time while the corrosion rates at 95% oxygen saturation were higher than at 40% saturation. All the indices indicated that the water with high oxygen content was more corrosive than the water with low oxygen content. The mean calculated CCPP values for water with 95% oxygen saturation was more negative than for water with 40% oxygen saturation thus indicating that the scale formation and protection was less likely to take place.

It is possible, however, that protection could take place as a result of the rapid formation of a protective coating of corrosion products.

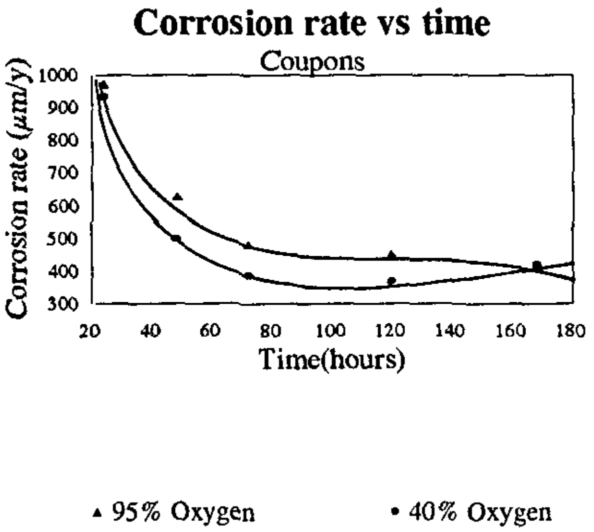


FIGURE 4.45: THE EFFECT OF HIGH AND LOW DISSOLVED OXYGEN CONTENT ON THE CORROSION RATE OF MILD STEEL

TABLE 4.5

CALCULATED INDICES VALUES FOR HIGH AND LOW DISSOLVED OXYGEN CONTENT

time:	Indices values at 95% O_2 Saturation								Indices values at 40% O_2 saturation							
hours	LSI	RSI	LI	DFI	AI	Y	RCI	CI	LSI	RSI	LI	DFI	AI	Y	RCI	CI
0	-0,93	9,6	0,35	0,24	11,3	73	18,4	0,37	-0,62	9,07	0,32	0,54	11,5	111	10,5	0,6
48	-1,40	10,39	0,47	0,08	10,8	41	41,0	0,16	-0,86	9,49	0,41	0,28	11,4	81	31,0	0,72
168	-1,56	10,49	0,46	0,06	10,6	36	30,2	0,23	-1,46	10,3	0,46	0,07	10,7	37	29,5	0,33

Observations from table above:

LSI > -0,5 corrosive; 95% and 40% saturation was corrosive but 95% was more corrosive than 40%.

RSI > 7 corrosive; the same as for the LSI

LI > 0,5 corrosive; 95% and 40% saturation was non-corrosive but 40% was less corrosive than 95%

DFI < 1 corrosive; the same as for the LSI

AI < 12 corrosive; the same as for the LSI

YI < 200 corrosive; the same as for the LSI

RCI > 26 corrosive; the same as for the LI

CI < 0,1 corrosive; the same as for the LI

4.2.5 Effect of linear flow rate

The flow rate in the two 80 mm ID pipe systems were controlled at 15,2 cm/sec or 9,12 m/min and 7,7 cm/sec or 4,5 m/min respectively. These flow rates were chosen arbitrary and not necessary equivalent to flow rates experienced in distribution or reticulation systems. Samples for chemical analysis were taken when the investigation commenced and then at 24 and 48 hour intervals for seven days. Corrosion rate measurements were taken at the same time.

RESULTS

Calculated indices values are shown in Table 4.6. Results of conductivity against time are graphically represented in Figure 4.46. Measured corrosion rates of the coupons are shown in Figure 4.47.

Alkalinity and calcium concentrations and conductivity decreased initially but levelled off after about 60 hours, At high flow rate the decrease was more rapid than at low flow rate. The measured corrosion rates of the coupons also showed an initial rapid decrease in corrosion rates tapering off towards a constant rate after about 80 hours with corrosion rates at high flow being higher than at low flow rates. Corrosion rates measured with the PVC.Carb.RE system and the corrater more or less followed the same pattern as changes in alkalinity. All the indices except for the RCI indicated that the water at high flow rate was more corrosive. Mean calculated CCPP values for the full duration of the investigation indicated higher negative values at high flow rate compared to low flow rate thus enhancing corrosion at higher flow rates. (Table 4.7). CCPP and Indices values are only dependent on the chemical composition of the water because the flow rate is not provided for in their equations.

4.2.6 Effect of temperature

The temperatures selected were a function of what could be achieved in the experimental set-up although it is also typical of water temperatures in reticulation systems. The heat generated by the submersible pump was used to maintain a temperature of 35°C in the first pipe system and the low temperature of 25°C was achieved by using an immersible cooler in the 200 litre container through which water was recirculated. Chemical adjustment of the water was done only after the water obtained the abovementioned temperatures. Samples for chemical analysis and corrosion rate measurements were taken at the start of the investigation and thereafter with one day intervals for seven days.

RESULT

Calculated indices are shown in Table 4.8. Measured corrosion rates are shown in Figure 4.48 for the coupons and Figure 4.49 for the PVC.Carb.RE system.

The initial alkalinity and calcium concentrations and conductivity decreased during the first 20 to 50 hours where after it increased. The measured corrosion rates decreased with time while the corrosion rates at 35°C were higher than the corrosion rates for 25°C (Figures 4.48 and 4.49). The calculated indices indicated more corrosive water

TABLE 4.6

CALCULATED INDICES VALUES FOR HIGH AND LOW FLOW RATES

time:	Indices values for flow rate of 15,2 cm/sec								Indices values for flow rate of 7,7 cm/sec							
hours	LSI	RSI	LI	DFI	AI	Y	RCI	CI	LSI	RSI	LI	DFI	AI	Y	RCI	CI
0	-0,73	9,36	0,35	0,39	11,5	102	16,7	0,46	-0,66	9,22	0,33	0,45	11,6	115	18,2	0,58
48	-1,03	9,93	0,46	0,19	11,2	62	29,0	0,26	-0,67	9,35	0,35	0,44	11,5	112	16,1	0,40
168	-1,43	10,37	0,48	0,08	10,8	40	10,4	0,23	-0,90	9,59	0,36	0,26	11,3	76	19,6	0,43

Observations from table above:

LSI > -0,5 corrosive; 15,2 cm/sec and 7,7 cm/sec corrosive but 15,2 cm/sec is more corrosive than 7,7 cm/sec.

RSI > 7 corrosive; the same as for the LSI

LI > 0,5 corrosive; non-corrosive but 7,7 cm/sec is less corrosive than 15,2 cm/sec.

DFI < 1 corrosive; the same as for the LSI

AI < 12 corrosive; the same as for the LSI

YI < 200 corrosive; the same as for the LSI

RCI > 26 corrosive; non-corrosive but 15,2 cm/sec less corrosive than 7,7 cm/sec.

CI < 0,1 corrosive; non-corrosive but 7,7 cm/sec less corrosive than 15,2 cm/sec.

TABLE 4.7

CALCULATED CORROSION RATES AND CCPP VALUES FOR HIGH AND LOW FLOW RATES

Flow rate	15,2 cm/sec				7,7 cm/sec			
time:hours	CR-prog μm/y	CR-TDS μm/y	CR-Cond μm/y	CCPP μm/y	CR-Prog μm/y	CR-TDS μm/y	CR-Cond μm/y	CCPP μm/y
0	228,7	212,2	213,1	-1,93	242,8	225,4	225,9	-1,531
24	210,8	206,3	206,7	-2,89	249,9	212,2	213,1	-0,639
48	176,6	161,0	161,9	-3,17	230,0	212,2	213,1	-1,308
72	168,2	161,0	161,9	-6.03	231,0	212,2	213,1	-1,529
120	169,5	147,8	149,1	-5.02	228,4	212,2	213,1	-1,084
168	163,4	147,8	149,1	-7,17	224,2	200,8	200,3	-3.471

Mean CCPP value for 15,2 cm/sec flow rate was, -4,37 mg/ℓ $CaCO_3$

Mean CCPP value for 7,7 cm/sec flow rate was, -1,59 mg/ℓ $CaCO_3$

at 35°C for the LSI and RSI than for 25°C while all the other indices indicated more corrosive water at 25°C than at 35°C. The reason for this tendency may be the fact that the effect of temperature is only incorporated in the LSI and RSI equations and not into the equations of the other indices.

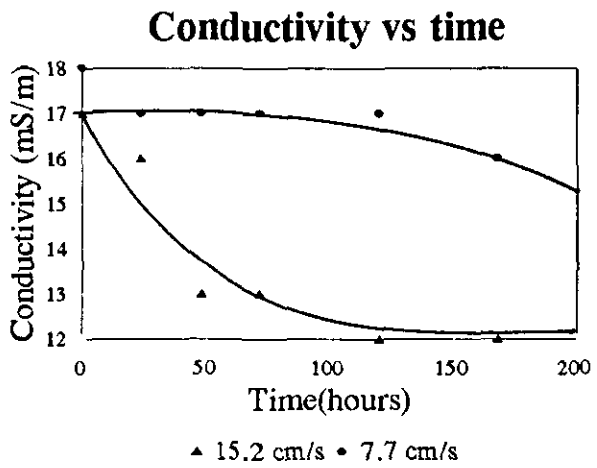


FIGURE 4.46

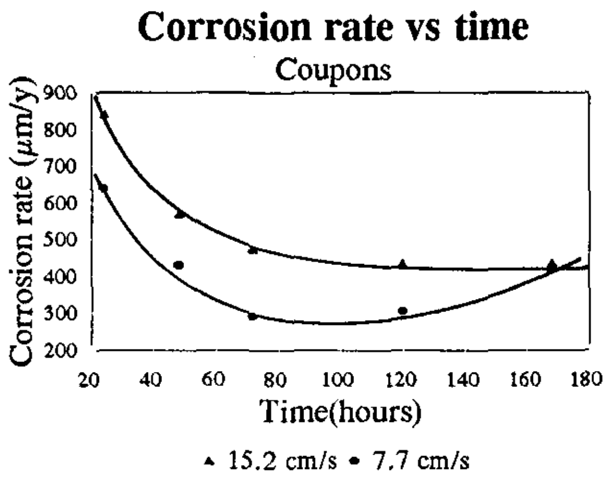


FIGURE 4.47

FIGURE 4.46 AND 4.47: CHANGES IN CONDUCTIVITY AND THE EFFECT OF HIGH AND LOW FLOW RATES ON THE CORROSION OF MILD STEEL.

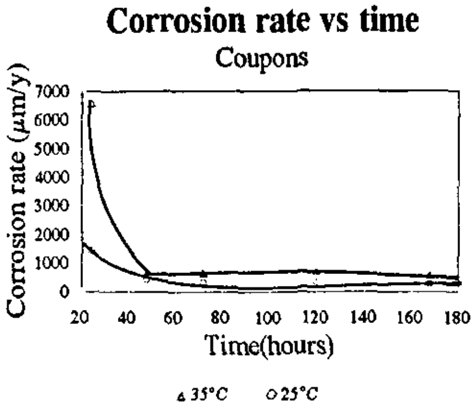


FIGURE 4.48

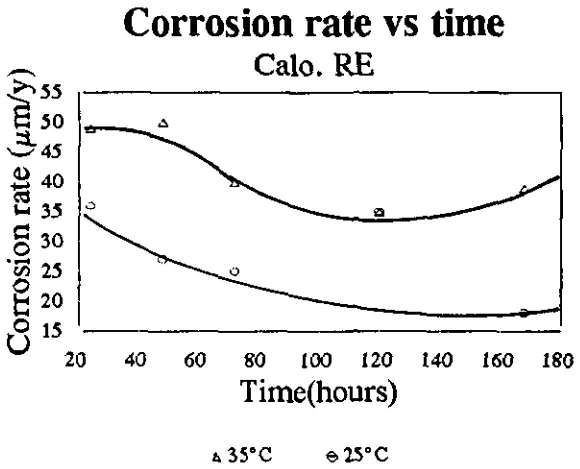


FIGURE 4.49

FIGURE 4.48 AND 4.49 **THE EFFECT OF HIGH AND LOW TEMPERATURE ON THE CORROSION MEASURED WITH COUPONS AND ELECTRODE SYSTEMS OF MILD STEEL**

TABLE 4.8

CALCULATED INDICES VALUES FOR HIGH AND LOW TEMPERATURES

time:	Indices values for 35°C								Indices values for 25°C							
hours	LSI	RSI	LI	DFI	AI	Y	RCI	CI	LSI	RSI	LI	DFI	AI	Y	RCI	CI
0	-0,72	9,13	0,37	0,34	11,16	67	16,22	0,32	-0,48	8,96	0,32	0,66	11,66	143	18,20	0,56
48	-0,67	9,25	0,45	0,38	11,21	71	29,16	0,25	-1,35	10,33	0,53	0,09	10,76	40	24,81	0,22
168	-0,42	8,87	0,40	0,68	11,47	108	23,27	0,39	-0,97	9,78	0,45	0,22	11,15	62	19,4	0,28

Observations from table above:
LSI $> -0,5$ corrosive; 35°C and 35°C non-corrosive but 25°C is less corrosive than 35°C.

RSI > 7 corrosive; 35°C and 25°C corrosive but 35°C is more corrosive than 25°C.

LI $> 0,5$ corrosive; 35°C and 25°C non-corrosive but 35°C is less corrosive than 25°C.

DFI < 1 corrosive; 35°C and 25°C corrosive but 25°C is more corrosive than 35°C.

AI < 12 corrosive; the same as for the DFI

Y < 200 *corrosive; the same as for the DFI*

RCI > 26 corrosive; the same as for the DFI

CI $< 0,1$ corrosive; the same as for the LI

NB: Because no definite trend could be observed for any index versus time only the nearest two values for each index at 35°C were compared with the nearest two values for 25°C/

5. CORROSION MONITORING AND CONTROL IN DISTRIBUTION SYSTEM

5.1 SECONDARY TREATMENT

The aim of this study was to simulate conditions in which secondary treatment such as the addition of silicate or monochloramine could be evaluated in drinking water. For this purpose treated water was run continuously through a pipe system and selected chemicals added. Coupons were exposed for a total of eight weeks in the pipes before removal while the corrosion rate on electrodes were measured twice a week.

5.1.1 Effect of silicate

Corrosion rates of coupons were measured weekly for ten weeks. Freshly produced chlorinated potable water flowed continuously through three pipe systems. The first pipe system acted as a reference and respectively 5 mg/ℓ and 20 mg/ℓ of non- activated silicate were dosed continuously into the second and third pipe systems. A weekly composite water sample was obtained from each pipe system for chemical analysis.

Results for the measured corrosion rates are graphically represented in Figure 5.1 and Figure 5.2 for changes in conductivity. Measured corrosion rates were about the same for both 5 and 20 mg/ℓ SiO_2. The overall tendency, however, is that the corrosion rates followed the same decreasing tendency as the conductivity. Corrosion rates and conductivity for potable chlorinated water that was not treated with silicate were about the same as for silicate treated water. The decrease in conductivity of the potable water produced during this investigation could not be controlled.

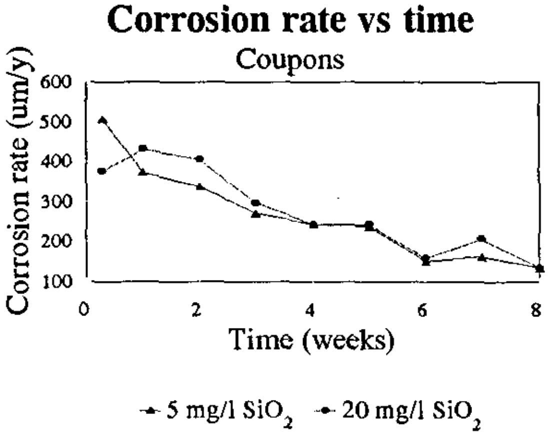


FIGURE 5.1 **THE EFFECT OF SILICATE AS SECONDARY TREATMENT ON THE CORROSION OF MILD STEEL IN CONTINUOUS FLOWING POTABLE WATER.**

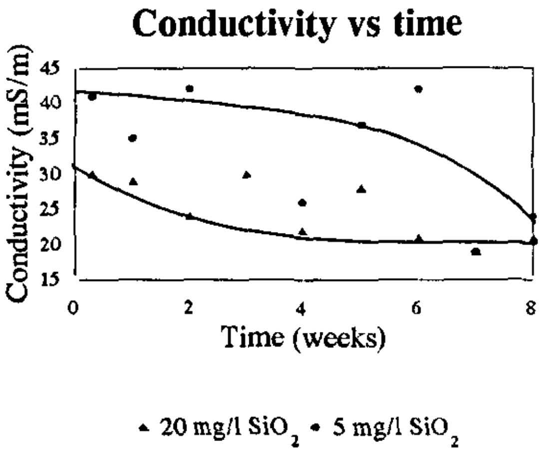


FIGURE 5.2 CHANGES IN CONDUCTIVITY OF POTABLE WATER DURING THE INVESTIGATION OF THE EFFECT OF SILICA AND MONOCHLORAMINE ON THE CORROSION OF MILD STEEL IN CONTINUOUS FLOWING POTABLE WATER

5.1.2 Effect of monochloramine

Corrosion rates were measured alternatively every four and three days for a total duration of about thirty four days. During each period of four and three days a composite of respectively twelve and nine small samples were obtained from the two pipe systems for chemical analysis. Freshly produced chlorinated potable water flowed continuously through the two pipe systems connected in series. Monochloramine was dosed into the second of these pipes. Monochloramine was obtained by dosing diluted ammonia NH_4OH into the connecting pipe between the first and second through flow systems. Concentrations of ammonia was controlled such that water in the second pipe system contained an average of about 0,1 mg/ℓ free chlorine and 1,2 mg/ℓ monochloramine. Results for conductivity and corrosion rates measurements are represented graphically in Figures 5.2 and 5.3.

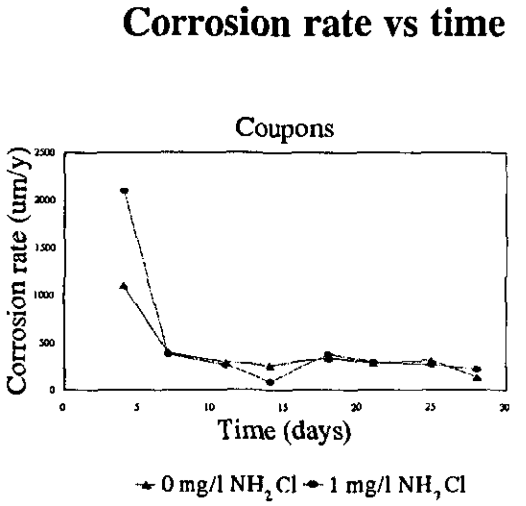


FIGURE 5.3 THE EFFECT OF MONOCHLORAMINE AS SECONDARY TREATMENT ON THE CORROSION OF MILD STEEL IN CONTINUOUS FLOWING POTABLE WATER.

From Figure 5.3 it can be seen that the corrosion rates were about the same for both chlorinated water and where 1 mg/ℓ NH_2Cl had been dosed after about seven days duration of the investigation.

As a result of the decrease in conductivity of the potable water, over which there was no control, it is possible that the inhibitory effect of either, the monochloramine or the silicate may have been masked. Ideal conditions would be where there is no change in conductivity and therefore the chemical composition of water which is known to effect corrosion rates of mild steel.

5.2 CONTINUOUS MONITORING IN DISTRIBUTION SYSTEMS

5.2.1 Before and after chlorination

Corrosion rates were measured in one through flow pipe system before chlorination after filtration and in another pipe system after chlorination. Measurements were conducted weekly on coupons and PVC.Carb.RE systems for fourteen weeks. The test continued for was eight weeks.

Results obtained are shown graphically in Figures 5.4 and 5.5 for the corrosion rates measured respectively on the coupons and the PVC.Carb.RE. Calculated corrosion rates are shown in Figure 5.6 and conductivity changes in Figure 5.7. Mean values for all the results were calculated for the last seven weeks of the experiment while each set of coupons had been exposed for eight weeks. The mean corrosion rates of the coupons and PVC.Carb.RE system obtained during the last seven weeks, as well as for the calculated corrosion rates, show higher corrosion rates for chlorinated water than for non-chlorinated water.

The indication that chlorine increases the corrosivity of potable water agrees with the results obtained in the six pipe system, paragraph 4.1.4.

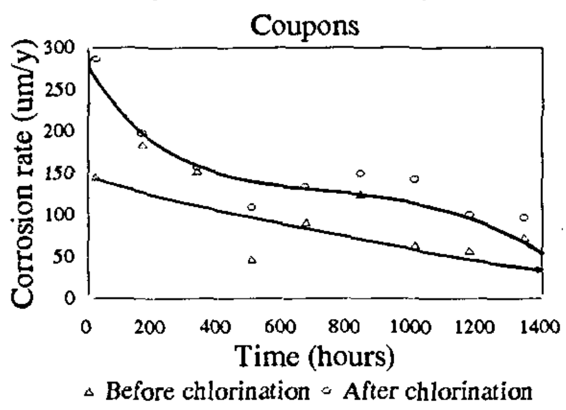


FIGURE 5.4 THE EFFECT OF CHLORINATED AND NON-CHLORINATED POTABLE WATER ON THE MEASURED CORROSION RATES OF MILD STEEL.

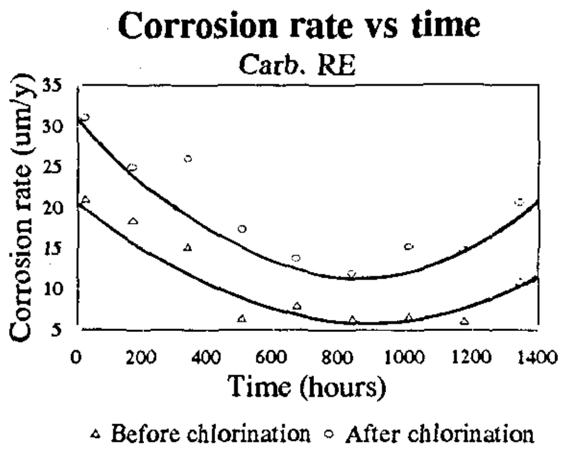


FIGURE 5.5 THE EFFECT OF CHLORINATED AND NON-CHLORINATED POTABLE WATER ON THE MEASURED CORROSION RATES OF MILD STEEL

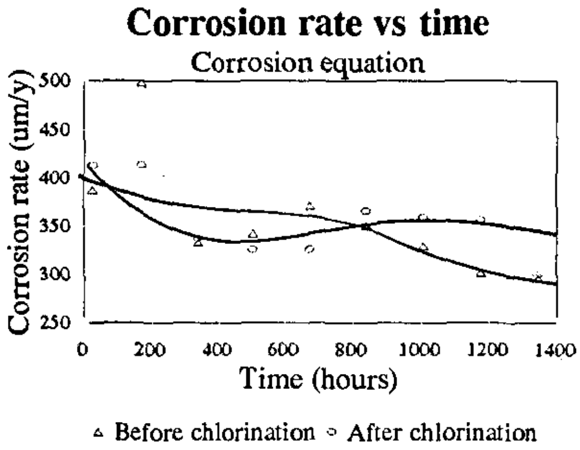


FIGURE 5.6 THE EFFECT OF CHLORINATED AND NON-CHLORINATED POTABLE WATER ON THE CALCULATED CORROSION RATES OF MILD STEEL

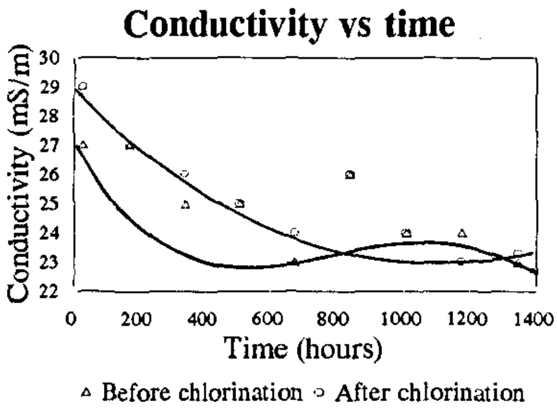


FIGURE 5.7 CONDUCTIVITY OF CHLORINATED AND NON-CHLORINATED POTABLE WATER IN THE DISTRIBUTION SYSTEM

6. DISCUSSION

6.1 EFFECTS OF DIFFERENT ENTITIES ON THE CORROSIVENESS OF STERKFONTEIN DAM WATER (LABORATORY INVESTIGATION)

From the preliminary investigation, paragraph 3.1.1 and the detailed discussion of the results obtained, Appendix C, it was concluded that the corrosivity predicted by none of the indices correlated with the measured corrosion rates on coupons for the different chemical species such as, chloride, sulphate, carbonate and calcium.

An important deduction, however, was that a relationship exists between the ionic strength, or conductivity, of the water and the measured corrosion rates.

A direct relationship between the conductivity of the water containing different chloride to sulphate ratios and corrosion rates were obtained, paragraph 3.1.2 and 3.4. Corrosion rates were high where chloride to sulphate ratios (high chloride concentration) and sulphate to chloride ratios (high sulphate concentration) were high. Conductivities were high in these instances, but low for those cases where the chloride as well as the sulphate concentrations were low. When the conductivity of these water samples were adapted with sodium acetate to the same level the measured corrosion rates for all these samples were about equal. **This reinforces the observation that corrosion rates are primary a function of ionic strength of the electrolyte.**

From these observations it was concluded that the initial corrosion rate was directly related to the contribution of chloride and sulphate to the water conductivity. A more thorough investigation followed, paragraph 3.5.1, in which the effect of chloride, sulphate, nitrate, bicarbonate, carbonate and hydroxide were investigated separately. Linear relationships were obtained between the measured corrosion rates and chloride, sulphate and bicarbonate ion concentration. A logarithmic relationship was obtained for hydroxide concentration for pH $>9,0$. Stone *et al.* (1987) also found increasing corrosion rate measurement for copper and zinc for increasing conductivity caused by increasing chloride, sulphate and bicarbonate concentrations. They also used the Linear Polarization technique for measuring corrosion rates.

The relationship between carbonate ion concentration and measured corrosion rates was not so clear, presumably because of the effect of hydroxide present on the corrosion rate. See detail discussion in Appendix D.

The laboratory investigation, paragraph 3.5.2, on the effect of bicarbonate was repeated at a pH 8,3 and 10 in the presence of calcium as calcium nitrate. Conductivity increased because of the calcium nitrate added into both the solutions, causing a corresponding increase in corrosion rates.

At pH 10 and increasing total carbonate concentration, the corrosion rate and conductivity of water samples containing calcium ions decreased. On the contrary the increasing conductivity and corrosion rates were observed for the same samples without calcium. The reason for this tendency was probably caused by a higher CO_3^{2-}/HCO_3^- ratio causing increasing amounts of calcium carbonate to precipitate in the samples containing calcium. This led to a decrease in the dissolved salt content and consequently the conductivity of the samples and therefore a related decrease in corrosion rates. It is, therefore necessary to incorporate the calcium carbonate precipitation potential (CCPP) in any equation expressing the combined effects of different parameters on the corrosion of mild steel. Other factors like chlorine and oxygen content, pH and temperature were also investigated, paragraphs 3.5.3 to 3.55. **Linear relationships between the corrosion rates and increasing chlorine concentration, oxygen content and temperature as well as pH in the pH range 6,5 to 9,0 were found.**

The development and evaluation of a corrosion equation called the Conductivity based Corrosion Equation (C-Rate) with the following form,

$$CR = [aC\ell^- + b\,SO_4^{2-} + c\,NO_3^- + d\,C\ell_2 + e\,(Talk - \frac{CCPP}{F_1}) + f\,pH - g]F_1F_2$$

is discussed in Appendix E. This equation can be applied to potable water if data on chloride, sulphate, nitrate, chlorine, Talk, CCPP, pH oxygen and temperature are available. From the latter analysis the CCPP value can be obtained by making use of the JTG computer program, Appendix G, or the Stasoft III program. A laboratory analytical method, Appendix H, may be used if the computer programs are not available. The corrosion rates, in microns per year, calculated with the C-Rate can be evaluated by comparing it to the Middelsex Index, Appendix H. It is, however, important to remember that the C-Rate predicts the initial corrosiveness of water for uniformly corroded mild steel and only for those chemical entities appearing in the equation. For positive CCPP values it is also important to note that although the water may be highly corrosive according to the equation, the corrosive effect may be neutralised by the precipitation of calcium carbonate.

6.2 EFFECT OF ALKALINITY INVESTIGATED IN THE SIX PIPE THROUGH FLOW SYSTEM

In this investigation it was observed that the corrosion rate of mild steel increased with increasing alkalinity, and negative CCPP values. This tendency could be related to an increase in conductivity because of an increase in alkalinity. At increasing positive CCPP values and constant alkalinity the corrosion rate decreased, probably because calcium carbonate precipitated causing a decrease in conductivity and a related decrease in corrosion rates. In this regard the observations made in this investigation coincided with the laboratory observations discussed in paragraphs, 3.1.1 and 3.5.2.

The calculated indices as a function of CCPP shown in paragraph 4.1.1, indicated that water will be non-corrosive when the values are:

Calculated index value		:	Corresponding CCP value
LSI	$> -0,5$	:	CCPP > 0
RSI	$> 7,0$	:	CCPP $> 19,0$
LI	$> 5,0$	:	CCPP $> 2,5$
DFI	$> 1,0$	:	CCPP $> 1,0$

RCI 5 to 25 : -6,7 > CCPP <0
<5 : CCPP >0 scale formation
CI > 0,1 : CCPP all values negative and positive
AI >12 : CCPP > 2,0
YI > 500 : CCPP > 4,5

From these results it can be concluded that all the indices, except the Casil Index, indicated non-corrosive water if CCPP was positive and thus coincided with the decreasing measured and calculated corrosion rates obtained at all positive CCPP values. If the Ryznar Index is used as an indication of corrosiveness it may probably, according to the results above, cause an excessive precipitation of calcium carbonate in household appliances like geysers and kettles. By comparing the CCPP values shown above with all the other parameters, the chemical composition of potable water with good corrosion protection properties may be as given in the table below. From the investigation on the effect of negative and positive CCPP values on the corrosion rates and calculated indices it was clear that most indices indicated non corrosive water (formation of a protective $CaCO_3$ scale) for CCPP values ≥ zero. The RCI, however, predicted non-corrosive water for CCPP values above 19,0 mg/ℓ as $CaCO_3$. The CI gave scattered results.

TABLE 6.1 CHEMICAL ANALYSES OF A STABLE LOW CORROSIVE WATER

ANALYSES	RANGE
Conductivity mS/m	14,5 - 17,0
pH	8,3 - 8,6
TDS mg/ℓ	97,4 - 116
Alkalinity as mg/ℓ $CaCO_3$	71 - 89
Hardness as mg/ℓ $CaCO_3$	69 - 73
Calcium mg/ℓ	19 - 25
Magnesium mg/ℓ	2,6 - 3,4
Sodium mg/ℓ	3,9 - 10,0
Iron mg/ℓ	0,05 - 0,61
Activated SiO_2 mg/ℓ	4,0 - 9,6
Total SiO_2 mg/ℓ	9,0 - 10,0
Ammonia mg/ℓ	<0,05
Nitrite-N mg/ℓ	<0,30
Nitrate-N mg/ℓ	0,11 - 0,69
Sulphate mg/ℓ	<5
Chloride mg/ℓ	<5

6.3 THE EFFECT OF CHLORIDE

A direct relationship exists between the concentration of chloride and the measured corrosion rates. This was found in the laboratory investigation, paragraphs 3.1.1, 3.4 and 3.5.1.

Results from the two pipe system (paragraph 4.2.1) also indicated that water with high chloride levels was more corrosive than water with low chloride content. In the last case it was, however, observed that the corrosion rates for the coupons, Calo.RE and corrosion equations (C-Rate) tended to increase again after about 200 hours exposure time.

The initial decrease in pH observed can be related to a decrease in alkalinity caused by $CaCO_3$ precipitation. Increased corrosion rates after 24 and 200 hours at low and high chloride dosages may be caused by turbucle formation, which is a phenomena occurring in water with pH >7,5 (See Appendix A paragraph 1.4.1). In water containing high chloride concentration the pH increased more rapidly as was the case in water with low chloride content. This probably caused turbucles to form more rapidly with a consequent increase in corrosion rate.

The Larzon, Riddick Corrosion and Casil indices indicated that the water with high chloride content was more corrosive than the water with low chloride content. The Feigenbaum Index initially indicated a lower corrosiveness for water with high chloride content than for low chloride content.

6.4 THE EFFECT OF SULPHATE

As was the case at chloride, sulphate (paragraph 3.1.1, 3.4, 3.5.1 and 4.2.2) also causes higher corrosion rates at increasing dosages. Initially a decrease in corrosion rates occurred followed by an increase in corrosion rates probably caused by turbucle formation (See Appendix A paragraph 1.4.1).

The Larson Index and Casil Index indicated higher corrosiveness for water with high sulphate content, while the Feigenbaum Index indicated lower corrosiveness. These indices, however did not predict the increase in corrosiveness after an initial decrease.

6.5 EFFECT OF SILICATE

From the investigation done on the effect of silicate, paragraph 4.1.2, it can be seen that the conductivity, alkalinity as well as the silicate concentration decreased with time and eventually reached a constant value. The decrease in alkalinity and conductivity may be due to the formation of calcium carbonate precipitates while the decrease in silicate may be as a result of the silicate combining with the corrosion scale. Corrosion rates measured on coupons indicated that waters to which respectively 5 and 20 mg/ℓ SiO_2 added were less corrosive than the neat Sterkfontein Dam water after 60 hours. The corrosion rates in water to which 20 mg/ℓ SiO_2 was added was higher than water with a 5 mg/ℓ dosage.

Graphical representation of corrosion rates for the coupons, and PVC.Carb.RE system versus SiO_2 concentration indicated a decrease in corrosion rates of coupons where the SiO_2 concentration was 2 - 8 mg/ℓ and for PVC.Carb.RE where the SiO_2 concentration was 2 - 10 mg/ℓ. The corrosion rates on both the coupons and the PVC.Carb.RE increased when the SiO_2 concentration exceeded respectively 10 and 12 mg/ℓ SiO_2

Corrosion rate tendencies obtained with the coupons, corrater and PVC.Carb.RE system for high and low non-activated silicate concentration, (paragraph 4.2.3) followed the same pattern as the alkalinity and conductivity versus time. The corrosion rates after dosing 50 mg/ℓ SiO_2 was higher than water with no SiO_2 added. This may be due to the higher conductivity, caused by a higher alkalinity in the water with high silicate content. If the higher alkalinity (hydroxide ions) at 50 mg/ℓ SiO_2 dosage was caused by hydrolyses of sodium silicate by way of the reaction,

$$Na_2SiO_3 + 2H_2O \rightarrow NaOH + H_2SiO_3$$

it could also explain the increase in corrosion rates, observed at silicate dosages greater than 10 to 12 mg/ℓ SiO_2 in the six pipe system (paragraph 4.1.2).

The RCI, CI and LSI in the two pipe system again indicated decreasing corrosion rates for increasing silicate dosages. **It thus appeared that silicate only acted as an inhibitor at dosages between 2 and 12 mg/ℓ as SiO_2. Very high silicate dosages, or associated chemicals, promoted corrosion.**

Comparing activated and non-activated silicate, it was found that the Calo.RE and coupons indicated higher corrosion rates for activated than for non-activated silicate although this effect was not so prominent for the coupons. These observations were in line with the tendency observed for conductivity (paragraph 4.2.3[b]). In this case the conductivity of activated silicate treated water was higher than water with non-activated silicate.

The CI and RCI indicated that both waters with non-activated and activated silicate were non-corrosive or scale forming.

6.6 EFFECT OF ORGANIC COAGULANTS

It was not possible to determine precisely what the effect organic coagulants had on the corrosion of mild steel, paragraph 4.1.3.

The alkalinity and conductivity of conditioned Sterkfontein Dam water while recirculating through the pipe system decreased with time. The values for these determinants in Sterkfontein Dam water with 4 mg/ℓ coagulant dosage being a bit higher than conditioned Sterkfontein Dam water with no organic coagulants and water with 10 mg/ℓ coagulant dosage, the highest. The calculated and measured corrosion rates showed the same tendencies as the tendencies for alkalinity and conductivity.

From the laboratory investigation, paragraph 3.5.6, it followed, that the addition of coagulants will;

a) Increase the corrosiveness of water (deionised water) containing no suspended matter and dissolved solids because the coagulant increases the conductivity of the water.

b) Have no effect on the corrosiveness of water (Vaal Dam water) containing suspended matter and dissolved solids (alkalinity and calcium) because the coagulant will be removed from this water due to floc formation.

6.7 THE EFFECT OF CHLORINE

Although the initial chlorine analysis of water to which chlorine had been added correlated well with the dosed amounts, e.g. 1, 5 and 10 mg/ℓ as $C\ell_2$, no chlorine could be detected after 24 hours. This observation indicated that the chlorine reacted with oxidisable matter in the water or dissipated.

The conductivity for water dosed with 1, 5 and 10 mg/ℓ chlorine was higher than the conductivity of Sterkfontein Dam water without chlorine dosage. Calcium concentration decreased more drastically in the Sterkfontein Dam water of which the alkalinity had been adjusted without any chlorine dosage, than water into which chlorine was dosed. In the latter case chlorine led to hydrochloric acid formation and a consequent decrease in pH resulting in a higher solubility for calcium carbonate. The more drastic decrease in alkalinity of water at high chlorine dosages could have been caused by alkalinity reacting with HCl formed when chlorine hydrolysed in water. Average pH for water with zero chlorine dosages was 7,8 and respectively 7,74; 7,27 and 7,33 for chlorine dosages of 1,0; 5,0 and 10,0 mg/ℓ.

The corrosion rates of the coupons decreased during the first 70 hours, whereafter it increased. Corrosion rates of water with chlorine was lower than those waters without chlorine. This phenomena could probably be explained as follows. During the first 70 hours the pH and alkalinity decreased indicating the formation of $CaCO_3$ scale resulting in lower corrosivity. After 70 hours the corrosion rates increased again but more drastically in Sterkfontein Dam water to which alkalinity without chlorine and with 1 mg/ℓ chlorine was added. At that stage the corrosion rate of water containing 5 and 10 mg/ℓ was the lowest. From the change in pH it can be seen that in the first two examples the average pH after 70 hours was higher than pH 7,4 and the latter two examples below pH 7,4. The higher corrosion rates in the first two examples were probably caused by the chemical formation of turbercules which is a phenomena observed only at pH $>$ 7,4 (Appendix A, paragraph 1.4.1 (c) (iv). Turbercule formation could not occur in the last two examples because the pH was below 7,4. However, the minor increases in corrosion rates may have been caused by the loss of the protective $CaCO_3$ layer being dissolved as a consequence of the lower pH ($<$7,4). **Results obtained during the continuous monitoring (paragraph 5.2) of the effect of chlorine, indicated higher measured and calculated corrosion rates for water containing chlorine (≈ 1,2 mg/ℓ as $C\ell_2$) compared to unchlorinated water.** This tendency may be due to the presence of hydrochloric and hypochlorous acid, formed by chlorine, with a resultant lower pH. The mean pH, for the duration of this investigation, was lower (pH 7,9) in water with chlorine than in water without chlorine (pH 8,2). For both waters the corrosion rate initially decreased during the first 500 hours, whereafter an increase was observe. This tendency may be caused by turbucle formation, because in both waters the pH was higher than 7,5 for the duration of this investigation.

6.8 THE EFFECT OF MONOCHLORAMINE

From the results in paragraph 4.1.5 it follows that monochloramine may act as an corrosion inhibitor at dosages between 1 and 5 mg/ℓ, but promote corrosion at dosages higher than 5 mg/ℓ. When applied as secondary disinfectant, paragraph 5.1.2 the effect was not so clear.

6.9 THE EFFECT OF OXYGEN

All the measured corrosion rates (paragraph 4.2.4) at 95% oxygen saturation were higher than at 40% oxygen saturation. All the indices also indicated that water with high oxygen content was more corrosive than water with low oxygen content.

6.10 THE EFFECT OF FLOW RATE

Measured corrosion rates were higher at the high flow rate than at the low flow rate. However, calculated corrosion rates were higher for low flow rates than high flow rates. These contradictory results can probably be explained as follows. At a high flow rate it was observed that the alkalinity and calcium concentrations (formation of $CaCO_3$) as well as the conductivity decreases much more rapid than was the case at a low flow rate, indicating a more rapid depletion of alkalinity from solution therefore inducing higher corrosion rates at high flow rate. This higher corrosion rate on coupons may be caused by a higher rate of oxygen supply to the cathodic surface, causing hydroxide formation and a consequent formation of $CaCO_3$. Calcium carbonate that combined with the hydroxide layer would come from alkalinity. $CaCO_3$ precipitating from solution resulting in a decrease in alkalinity.

After the initial period during which a high rate of corrosion is observed and the first protective layer of iron oxide and $CaCO_3$ have formed, the corrosion rate should decrease as the protective layer increases in thickness as more alkalinity precipitates from the solution.

The higher calculated corrosion rates obtained with the equation (C-Rate) at low flow rates compared to the high flow rates were caused by the effect of alkalinity on conductivity which was higher at low flow rate, than at high flow rate. Furthermore the equation is conductivity related and a factor for flow rate was not incorporated in the equation.

All the indices except for the RCI indicated higher corrosiveness at high flow rate than for low flow rate.

6.11 THE EFFECT OF TEMPERATURE

All the corrosion rate measuring techniques showed higher corrosion rates at 35 °C than at 25 °C. This observation coincided with the observation made in the laboratory investigation, paragraph 3.5.5, were it was **found that the corrosion rates increased linearly with an increase in temperature.** Of the indices only the LSI and the RSI indicated higher corrosion rates at 35 °C than at 25 °C because these indices are the only ones that make provision for temperature in their equations, see Appendix A, paragraph 5.1.

6.12 COMPARISON OF DIFFERENT CORROSION RATE MEASURING TECHNIQUES, CORROSION EQUATIONS AND INDICES.

The different ECI electrode systems are discussed in paragraph 2.1.3 page 7. These electrode systems are probes for the Calo.RE with calomel reference electrodes, Mild S.RE *probes with mild steel reference electrodes and* PVC.Carb.RE *probes with carbon* reference electrodes.

6.12.1 Comparison of different ECI electrode systems

From the study to determine the repeatability of corrosion rate measurements, paragraph 3.3.1, it was clear that the Calo.RE gave more repeatable readings, with a standard deviation of 7,45%, compared to the Mild S.RE which gave a deviation of 44,44%. The Carb.PVC.RE, developed by Rand Water, Calo.RE and Mild S.RE systems gave the same tendencies except for the Galv.RE which gave scattered results. See paragraph 2.1.3 and 3.4 for more details. The unreliable results obtained with the Mild S.RE may be related to the working electrode and mild steel reference electrode that corroded simultaneously. For this reason it was decided to use only the Calo.RE and PVC.Carb.RE systems. The Calo.RE was used in laboratory investigations while the PVC.Carb.RE was used for field investigations.

6.12.2 Comparison of corrosion rate measurements obtained with different measuring techniques

From the investigation of the effect of alkalinity on the corrosion rate of mild steel measure with the corrater, Calo.RE and PVC.Carb.RE systems, paragraph 4.1.1 it can be seen that all three systems followed the same tendencies. Where the CCPP values increased from negative to zero, corrosion rates increased as well, but decreased with increasing higher CCPP values (See Figure 4.3). Corrosion rate measurements on coupons where the CCPP values were negative did not show a definite pattern. However, for al positive CCPP values corrosion rates decreased, which agree with measurements done on the electrochemical corrosion measuring systems.

The tendencies observed for the measured corrosion rates, versus silica content in the six pipe system, paragraph 4.1.2, were the same for both the PVC.Carb.RE and coupons. In the two pipe system, paragraph 4.2.3, the corrater, Calo.RE, PVC.Carb.RE and coupons all gave higher corrosion rates for high silicate dosage than low silicate dosage, paragraph 4.2.3(a), although the difference was not so obvious with the coupons. The Calo.RE, PVC.Carb.RE corrater and coupons also indicated that in all cases the corrosion rates using activated silicate were higher than with non-activated silica, paragraph 4.2.3(b). Again the difference was not so obvious on the coupons.

In the case of organic coagulants the measured corrosion rates were affected by the conductivity of the water and not the coagulant dosage.

Studying the effect of different chlorine concentrations, paragraph 4.1.4 only the corrater indicated lower corrosion rates in water dosed with chlorine. This corresponds to results obtained with the coupons. The other electrochemical techniques did not show increased corrosion rates after 72 hours exposure time as was actually measured with the coupons.

In the case of monochloramine, paragraph 4.1.5, it was also observed, as was the case with chlorine, that only the corrater indicated lower corrosion rates as was measured on the coupons at 1 mg/ℓ dosage. The other electrochemical methods gave confusing results.

As was the case in the laboratory investigation with the corrater, corrosion rates measured with the coupons at high chloride and sulphate content, paragraph 4.2.1 and 4.2.2 were higher at high concentration than at low concentration. Only the Calo.RE indicated increasing corrosion rates for both chloride and sulphate, while the PVC.Carb.RE and corrater did not follow this tendency. In the case of sulphate the difference between high and low sulphate content was again not so obvious.

Higher corrosion rates were observed on the coupons and the PVC.Carb.RE at increasing oxygen saturation, paragraph 4.2.4 but the opposite tendency was observed with the corrater. The reason could be that the corrater was more sensitive for changes in conductivity as water saturated with oxygen had a higher initial conductivity than the water depleted of oxygen.

Decreasing corrosion rates relative to time were observed with the corrater, coupons and PVC.Carb.RE at higher flow rate, paragraph 4.2.5. Only the coupons consistently showed higher corrosion rates at high flow rates than at low flow rates. The higher corrosion rates measured by the PVC.Carb.RE and corrater were probably again related to a higher initial conductivity for water with lower flow rate.

All the measuring techniques showed higher corrosion rates at high temperature than at low temperature, paragraph 4.2.6, because the conductivity of water is higher at higher temperatures.

6.12.3 Comparison between results obtained with the corrosion rate equations and tendencies obtained with corrosion rate measuring techniques

The effect of alkalinity, paragraph 4.1.1, on the calculated corrosion rate showed tendencies that correlated with measurements done by of the corrater, Calo.RE and PVC.Carb.RE for all CCPP values. Scattered results, however, were obtained at negative CCPP values using the coupons.

The calculated corrosion rate tendencies in the silicate investigation, paragraph 4.1.2 followed the tendencies obseved for alkalinity and conductivity but did not agree to tendencies obtained for corrosive measurements on the PVC.Carb.RE and coupons. This may be due to the fact that no provision for silica was made in the equation.

In the case of organic coagulant, paragraph 4.1.3, tendencies for the calculated and coupon measured corrosion rates were the same and followed the conductivity of the water.

The effect of chlorine displayed tendencies for the calculated corrosion rates that were similar to the corrosion tendencies observed for the coupons, presumely because the effect of chlorine was provided for in the C-rate (Prog) equation.

The effect of chloride and sulphate, paragraph 4.2.1 and 4.2.2 followed the same tendencies for the calculated corrosion rate as those obtained for the coupons and Calo.RE system, most likely because provision was made for the effect of chloride and sulphate in the equation.

6.12.4 Indices

Indices investigated:
Ryznar Stability Index (RSI), Langelier Saturation Index (LSI), Aggressive Index (AI), Driving Force Index (DFI), Riddick Corrosive Index (RCI), Larson Index (LI), Feigenbaum, Gal-or, Yahalom combination (Y), Casil Index (CI), and Calcium Carbonate Presipitation Potential (CCPP).

The following observations were made from the results obtained with the calculated indices throughout the investigation. For increasing ion concentrations, including bicarbonate and calcium, the initial measured corrosion rates increased, probably due to of an increase in conductivity. Most of the indices also predicted increasing corrosiveness for chloride and sulphate dosages except for the AI which showed no sensitivity for either chloride and sulphate while the RCI showed no sensitivity towards sulphate. This is due to the fact that no term or factor compensating for chloride and sulphate are present in the AI and for sulphate in the RCI. The Y indicated tendencies opposite to those obtained for the measured corrosion rates, Appendix A, paragraph 5.7, because it is based on the assumption that chloride and sulphate assist in more dense calcium carbonate crystal growth, thus leading to better corrosion protection. Almost all the indices indicated decreasing corrosiveness at increasing calcium concentration and higher alkalinity because they predicted the formation of calcium carbonate scale that protects against corrosion. The Larson Index showed no calcium sensitivity because provision is not made for calcium in this equation. The RCI Index followed the same pattern as the measured corrosion rates as calcium content because calcium is reflected as hardness in the equation. The CI Index showed tendencies that were partly similar to the tendencies for the measured corrosion rates because it is based on the contribution of bicarbonate towards the corrosiveness of water. From this discussion it follows that most indices predicted what would happen in water after a period of time, e.q. formation of a protective scale whereby corrosion rates would decrease, but no single index fully described the initial corrosiveness of water.

It was also observed during the investigation that linear relationships exists between the conductivity of the water and the corrosion rate of mild steel, paragraph 3.4 and 3.5.1. Indices that reflect the effect of conductivity are the RSI, LSI, and DFI, (See Appendix C). The only index that showed decreasing corrosion rates at increasing silica content and increasing corrosion rates at increasing oxygen content was the Riddick Corrosion Index, paragraph 4.2.4, because provision was made for both silica and oxygen in the equation. From the investigation of the effect of negative and positive CCPP values on the corrosion rates and calculated indices, it was clear that most indices indicated non corrosive water (formation of a protective $CaCO_3$ scale) for CCPP values ≥ zero. The RCI, however predicted non-corrosive water for CCPP values above 19,0 mg/ℓ as $CaCO_3$ while the CI gave scattered results.

To predict the initial corrosiveness of water three equations were developed by Rand Water. These three equations are as follows:

$$\mathrm{CRm} = [4{,}09\ \mathrm{Cl}^{-} + 4{,}0\ \mathrm{SO}_4^{2-} + 2{,}79\ \mathrm{Cl}_2 + 9{,}78\ \mathrm{NO_3\text{-}N} + 3{,}12\ \{T_{alk}\ \text{-}\mathrm{CCPP}/F_1\} + 9{,}98\ \mathrm{pH} - 118]F_1F_2 \quad \ldots\ 6.1$$

$$\mathrm{CRm} = 12{,}9\ \mathrm{mS/m} - 4{,}74 \quad \ldots\ 6.2$$

$$\mathrm{CRm} = 1{,}9\ \mathrm{TDS} - 3{,}84 \quad \ldots\ 6.3$$

Equation 6.1 is partly based on the conductivity of the water which is influence by the dissolved salt content that will determine the corrosiveness as well as the protective properties of water.

Equation 6.2 can be used to determine the corrosion rate of mild steel in potable water if the conductivity is known and equation 6.3 if the total dissolved solids (TDS) is known. To evaluate the results obtained with the latter two equations the key, shown below may be used.

KEY TO THE CALCULATED CORROSION RATES PRODUCED

The calculated result can now be compared with the Middelsex Water Company's index;

Corrosion Rate	Water Quality
• <51 micron (μm) per year	indicates both excellent water quality and pipeline protection
• 51 - 127 micron (μm) per year	indicates good water quality and protection
• 127 - 254 micron (μm) per year	indicates water of acceptable quality
• >250 micron (μm) per year	indicates corrosive water

If this index indicates a water that is corrosive but with a positive CCPP value, pipe protection will still be provided due to the precipitation of $CaCO_3$.

The effect of calcium carbonate on the conductivity, or corrosiveness of water, when precipitation takes place in over saturated water or dissolved when under saturated, is also incorporated in the equation. The effect of pH, temperature and oxygen content are also considered. Calculated values for this equation or index are given directly in micron per year (μm/y) which can be compared with the key above, (See Appendix H), that will indicate the corrosiveness as well as the protective properties of the water.

7. CONCLUSIONS

7.1 MEASURING TECHNIQUES

7.1.1 Conductivity significantly influences corrosion rate measurements.

All results indicated that the electrical conductivity of water plays a significant role in the corrosiveness of water. Therefore, any results obtained with an instrument relying on conductivity, such as the Corrater 1120 and the Schlumberger ECI 1286 will be proportional to the conductivity of the water or the electrolyte.

7.1.2 Evenly corroded working electrodes gave more reliable readings than clean, polished working electrode surfaces.

Care must be exercised in preparation of the surface condition of mild steel electrodes. Evenly corroded surfaces will give more stable readings than clean, polished electrodes.

7.1.3 The best reliable corrosion rate reading were obtained with PVC.Carb.RE probes.

More reliable readings were obtained with PVC.Carb.RE than with Mild S.RE probes. PVC reducing bush probes containing carbon reference electrodes used in the through flow systems, gave more reliable readings than galvanised reducing bush probes with mild steel acting as the reference electrode. Probes with calomel reference electrodes also gave more reliable readings than the galvanised reducing bush probes.

7.1.4 Results obtained with coupons although time consuming give a better indication of the corrosion process than that obtained with the electrochemical techniques.

Although the use of corrosion coupons made from the material to be investigated is time consuming and labour intensive it remains the only method by which accurate results can be obtained.

The electrochemical techniques used to test the effects of corrosion have more application where an accurate indication of how an electrolyte will react towards different metals or, how a specific metal will react towards different electrolytes.

7.2 CHEMICAL ANALYSIS OF A STABLE, LOW CORROSIVE WATER

Based on the extensive chemical and physical tests it was possible to characterise the chemical composition of a stable, low corrosive water. These analysis are shown in Table 7.1.

TABLE 7.1 CHEMICAL ANALYSES OF A STABLE LOW CORROSIVE WATER

ANALYSES	RANGE
Conductivity mS/m	14,5 - 17,0
pH	8,3 - 8,6
TDS mg/ℓ	97,4 - 116
Alkalinity as mg/ℓ $CaCO_3$	71 - 89
Hardness as mg/ℓ $CaCO_3$	69 - 73
Calcium mg/ℓ	19 - 25
Magnesium mg/ℓ	2,6 - 3,4
Sodium mg/ℓ	3,9 - 10,0
Iron mg/ℓ	0,05 - 0,61
Activated SiO_2 mg/ℓ	4,0 - 9,6
Total SiO_2 mg/ℓ	9,0 - 10,0
Ammonia mg/ℓ	<0,05
Nitrite-N mg/ℓ	<0,30
Nitrate-N mg/ℓ	0,11 - 0,69
Sulphate mg/ℓ	<5
Chloride mg/ℓ	<5

7.3 RELATIONSHIP BETWEEN THE FACTORS AND TERMS INCORPORATED IN "CORROSIVE INDICES" AND THE VALUE OF PREDICTIONS

Most of the "indices" are based on the calcium carbonate dissolution equilibrium and can for this reason be used to predict whether calcium carbonate will precipitate or dissolve in a specific water. Indices that are based on the calcium carbonate equilibrium are the Langelier Saturation Index, (LSI), Ryznar Stability Index (RSI), Driving Force Index (DFI), Aggressive Index (AI), and the Calcium Carbonate Precipitation Potential (CCPP). These indices are **not corrosion indices** but can be used to indicate the possibility of $CaCO_3$ precipitating from the water, in which case corrosion protection may occur. The equation to calculate the **Calcium Carbonate Precipitation Potential (CCPP)** is, however, **the only "index" with which the precise amount of $CaCO_3$ in mg/ℓ, that may precipitate or dissolve, as well as the equilibrium alkalinity and pH can be calculated.** The principal captured in the CCPP equation is applied in a practical manner in the marble test in which the potential of $CaCO_3$ being precipitated or dissolved is measured (See Appendix H). No sophisticated laboratory equipment is required for this test.

Other indices like the Riddick Corrosion Index (RCI), Larson Index (LI), Casil Index (CI) and Feigenbaum, Gal-or, Yahalom (Y) incorporate factors or terms to compensate for the effect of other compounds that may effect the corrosion process. For that reason these latter indices may be more applicable as corrosion indices, especially under specific conditions. Further remarks concerning individual indices are:

Langelier Saturation Index (LSI):	Only applicable in the pH range 6 to 9, but not applicable for soft water containing no calcium.
Ryznar Stability Index (RSI):	Probably only applicable to cooling tower and boiler waters, but not for potable water.
Aggressive Index (AI):	Only applicable for predicting the aggressiveness of water towards asbestos - cement pipes.
Driving Force Index (DFI):	Predicting the calcium saturation state of water.
Larson Index (LI):	General known as the Corrosion Index because it also makes provision for the effect of chloride and sulphate in its equation.
Riddick Corrosion Index (RCI):	This is the only index that is named a corrosion index, probably because it not only incorporates the effect of alkalinity and hardness but also the effect of oxygen and free CO_2. Most important is the fact that it also caters for the inhibiting effect of silica.
Casil Index (CI):	Ionic strength (conductivity) will effect calculated values of this index and it is probably the most applicable index for determining the initial corrosivity of water. Corrosion predictions with the Casil Index relate to corrosion rates of water containing activated silica, probably because provision for the effect of silicate was made in the equation.
Feigenbaum, Gal-or, Yahalom (Y):	Applicable for predicting the corrosivity for water if old thick corrosion layers exist.

7.4 DIRECT RELATIONSHIPS WERE OBTAINED BETWEEN DIFFERENT CHEMICAL/PHYSICAL PROPERTIES OF WATER AND MEASURED CORROSION RATES.

Direct relationships between the corrosion rate of mild steel and the concentration of some chemical species, which effects the conductivity and salinity of water, were observed. The same observations were made for water temperature. From these results it was possible to develop three equations called the Conductivity Base

Corrosion Equations (C-Rate) with which the corrosion rate of mild steel can be calculated if the chemical analyses of water is known. Expected corrosion rates in micron per year (μm/y) may be calculated. The equations are designated C-Rate(Prog), C - Rate (Cond) and C-Rate (TDS) and the equations are as follows

C-Rate (Prog)
$Crm = [4.09\ Cl^- + 4,0\ SO_4^{2-} + 2,79\ Cl_2 + 9,78\ NO_3\text{-}N + 3,12\{T_{alk} - CCPP/F_1\} + 9,98\ pH - 118]F_1F_2$.

C-Rate (cond)
$CRm = 12,9\ mS/m - 4,74$

C-Rate (TDS)
$CRm = 1,9\ TDS - 3,84$.

To get an overall view of the scale forming or corrosive properties of water it is better to calculate the values for as many as possible of the indices and equations developed by Rand Water, provided that the required chemical analyses are available. For convenience and greater accuracy the computer programme included in this report may be used.

7.5 EFFECT OF FLOW RATE

It was found that higher flow rates caused higher corrosion rates. This effect was not incorporated into the corrosion equations because the linearity, if any, was not determined.

7.6 EFFECT OF CORROSION INHIBITORS

The use of silicates as corrosion inhibitors may be considered, as a decrease in corrosion rates of mild steel were observed with silicate dosages up to 12 mg/ℓ as SiO_2. The use of non-activated silicates lead to a decrease in corrosion rates compared to the use of activated silicate which lead to an increase in corrosion rates at similar concentrations.

Monochloramine was found to decrease the corrosion rates at about 1 mg/ℓ concentration.

Due to experimental conditions which could not be controlled it was difficult to evaluate the use of either silicate or monochloramine as corrosion inhibitors in a distribution system. The conductivity of the water in which the tests were done gradually decreased during the eight weeks while the experiment lasted. As a result, the corrosiveness of the water decreased proportionally and the possible inhibiting effect of either silicate and monochloramine could have been masked.

8 RECOMMENDATIONS FOR FURTHER RESEARCH

1. FURTHER INVESTIGATION INTO THE INHIBITING EFFECT OF SILICATE AND MONOCHLORAMINE.

The inhibiting effect of silicate and monochloramine on the corrosiveness of water should be investigated further. Since monochloramine is already used as a disinfectant and formed in the water, it can easily be applied at the appropriate places in a distribution system and serve a dual purpose. In contrast to other inorganic chemical corrosion inhibitors such as the phosphate compounds, silicate does not present any health or environmental dangers, therefore, it's use to reduce corrosion should be further investigated. Furthermore silicate is already being used as a flocculant on some treatment plants.

2. RESEARCH ON METHODS TO PRODUCE WATER WITH SPECIFIC CHEMICAL AND PHYSICO/CHEMICAL PROPERTIES

Now that some guidelines are available to describe water which should not be corrosive or non-scale forming, more research can be done on methods to produce water with these qualities and methods to maintain these properties in long distribution systems.

3. RESEARCH TO BE DONE TO DEVELOP RAPID METHODS TO DETERMINE CORROSIVENESS

Research should be done to develop rapid reliable methods which are not as sensitive to conductivity as the current electrochemical methods to determine the corrosiveness of water.

4. REPEAT A SIMILAR INVESTIGATION ON STAGNANT WATER

Research should be repeated on the same basis as was done in this investigation, but to study the effect of stagnant water such as in service reservoirs.

5. *RE-ASSESSMENT OF THE HEYNIKE REPORT/PRINCIPLES*

With the conclusions drawn from this investigation the report by J J C Heynike "The economic effects of the mineral content present in the Vaal River Barrage on the community of the PWVS-complex" (Heynike 1981) should be re-assessed.

APPENDIX A

LITERATURE SURVEY

AND

REFERENCES

APPENDIX A

PAGE

1. CORROSION OF MILD STEEL AND VARIABLES THAT EFFECT IT

1.1 INTRODUCTION

Corrosion can lead to the dissolution of mild steel, a material often used in water reticulation systems and may liberate lead, cadmium and other heavy metals in piping creating a health hazard (Kirmeyer & Logsden, 1983). Shorter distribution system life and increased pumping costs (higher pipe roughness) are caused by corrosion. Corrosion is an electrochemical process (Kirmeyer *et al.*, 1983). All components of a galvanic cell (anode, electron conductor, cathode, electrolyte) must be present for the process to proceed. Elimination of one or more of these components will therefore control corrosion. See figure A1. At the cathode the electrons (generated at the anode) pass from the metal (electron donor) to some chemical species (electron acceptor) in the water adjacent to the cathode, this is usually molecularly dissolved oxygen, if present. The reactions at the anode cause continuous dissolution of the metal (corrosion), or, may give rise to precipitation of scale over the anode and cathode, eventually stopping the corrosion process completely (passivation of the surface).

1.2 COMPOSITION OF CORROSION SCALES

The general composition of scale was described by Sontheimer, Kölle and Snoeyink (1981) on examining a particular scale found in a pipe 100 years old. The composition is depicted in figure A2. A notable feature is the shell like layer consisting of goethite (alpha-Fe OOH) and magnetite. This layer comprises corrosion products and precipitates as a calcium rich outer layer and an iron rich inner layer. The hard and impervious layer is found in most scales and is important in fixing the scale components to the metal surface. Inside the layer the scale is mainly siderite, goethite and lepidocrocite (gamma - Fe OOH), while the outer layer consists mainly of goethite and calcite.

1.3 PROTECTIVE ACTION OF SCALES

Many factors determine the effectiveness of an protective scale. It seems as though the quality of the scale is determined by its porosity although the effectiveness of attachment to the wall is also important (Feigenbaum *et al*, 1978). These two factors probably occur simultaneously. A method to quantitatively evaluate scales was developed by Feigenbaum *et al.*, (1978), using an impedance measurement cell. It was found that effective scales show high resistance and low capacitance and *vice versa* for less effective scales. The effect of porosity was studied using three types of scales:

- Compact scale (Dense layers of iron rich inner and calcium rich outer scales)
- Intermediate porosity scale
- Porous scale (porous calcium rich layer and highly porous needle like iron rich layer)

Tests showed that the higher porosity scales gave poorer protection as measured by the impedance. It is postulated that the reason for this is that the diffusion of oxygen through the pores is the determining factor.

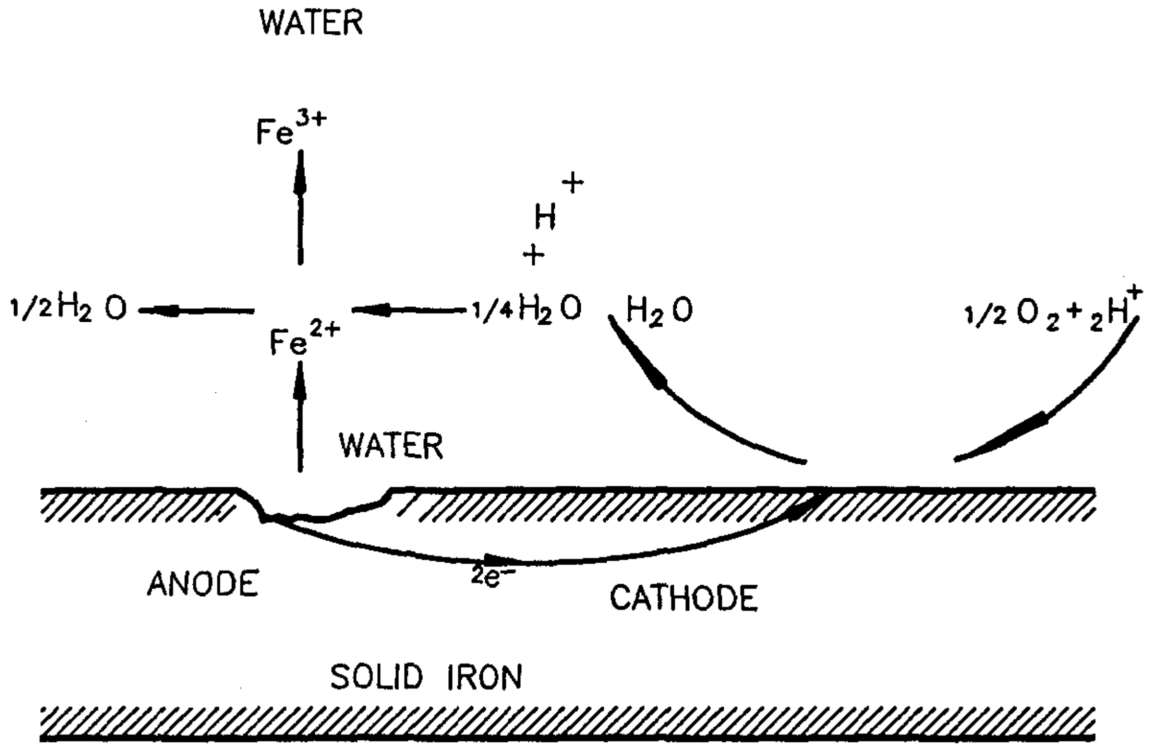


Figure A1 Fundamental corrosion reactions for cast–iron and mild steel pipes transporting drinking water

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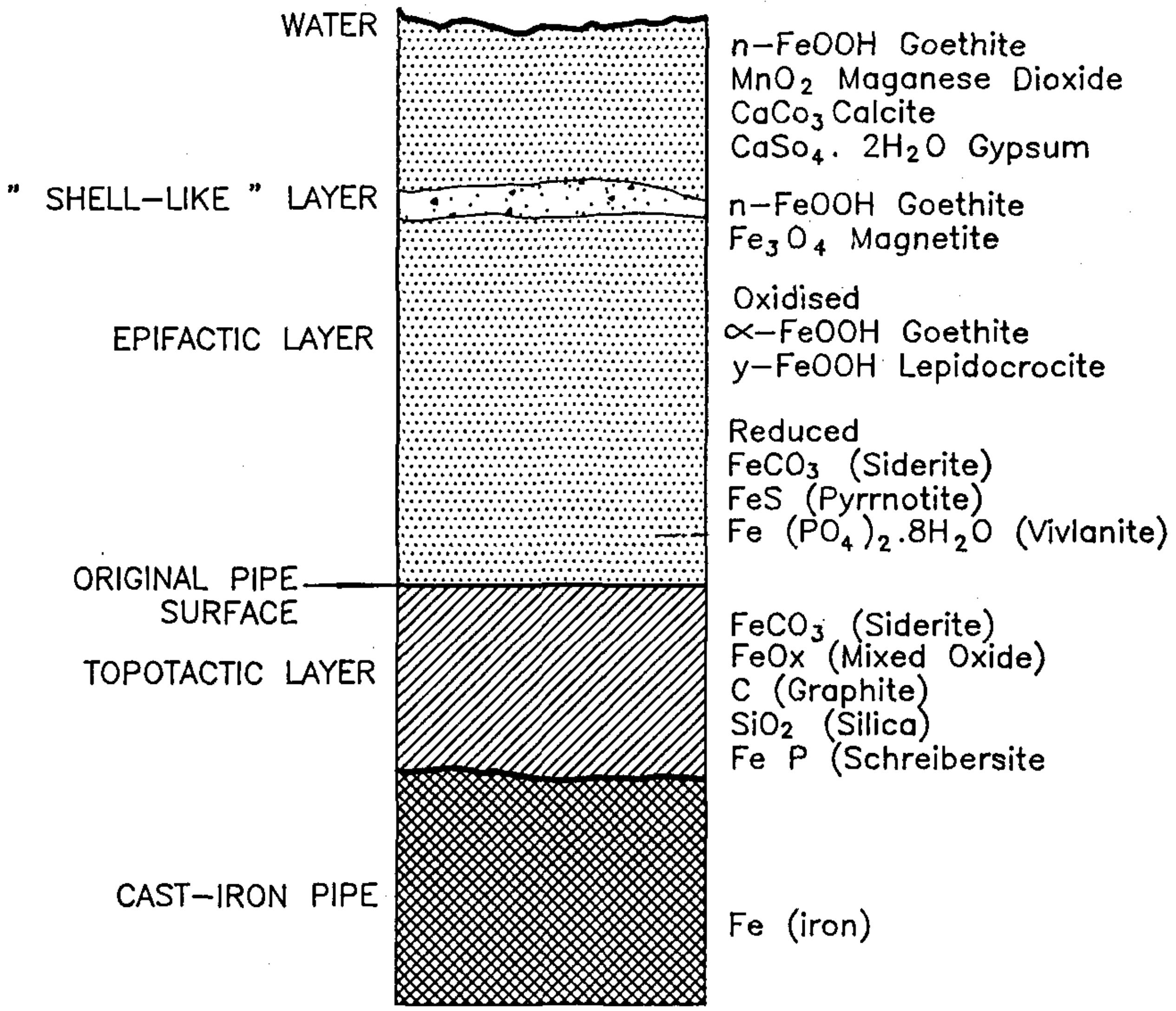

Figure A2 Schematic precentation of scale on a cast-iron distribution pipe

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In addition the composition of the scale was found to be important. Scales with high calcite content (Fe:Ca <3,9) gave good protection. When the calcite content was low the resistance of scale towards an electric current was determined chiefly by siderite content. Scales with high siderite content showed fairly high resistances, while low siderite - high magnetite containing scales, showed poor resistances. Goethite showed least resistance as predicted by McCauley *et al.*, (1958).

1.4 CORROSION REACTIONS

To understand the mechanism of corrosion and passivation it is necessary to review the various redox reactions and their consequences at the anode and cathode.

1.4.1 Anodic Reactions

a) Primary level corrosion reactions

At the anode, metal ions go into solution by oxidation of the solid iron, Fe,

$$Fe \rightarrow Fe^{2+} + 2e \quad \text{(A1)}$$

thereafter, alternative secondary and tertiary reactions can follow.

b) Secondary level anodic reactions

(i) The Fe^{2+} can precipitate in two ways, as $Fe(OH)_2$ and/or, as $FeCO_3$ (siderite) the latter when carbonate species are present in the water, i.e.

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ \quad \text{(A2)}$$

and/or

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 \downarrow \quad \text{(A3)}$$

There is no electron transfer in either of these reactions so that these can take place whether oxygen is present in the water above the anode or not.

(ii) If oxygen is present above the anode, Fe^{2+} can be oxidised to Fe^{3+}.

$$Fe^{2+} + \tfrac{1}{4}0_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2} H_20 \quad \text{(A4)}$$

The Fe^{3+} formed is then precipitated as $Fe(OH)_3$,

$$Fe^{3+} + 3H_20 \rightarrow Fe(OH)_{3(sol)} \downarrow + 3H^+ \quad \text{(A5)}$$

The overall reaction for precipitation of $Fe(OH)_3$ at the secondary level is

$$Fe^{2+} + \tfrac{1}{4}0_2 + {}^5/_2\, H_20 \rightarrow Fe(OH)_{3(sol)} + 2H^+ \quad \text{(A6)}$$

$Fe(OH)_2$ and $Fe(0H)_3$ precipitates are transit metastable solid states and exist, therefore, only as "fresh" precipitates. Both are precursors to the thermodynamically stable iron oxides and for this reason exist in a pseudo equilibrium state with respect to the dissolved species.

c) Tertiary level anodic reactions

Diagrams of redox potential, plotted as the negative logarithm of the electron activity (pe) against pH, gives the stable phase at each combination and pH. Such diagrams are called Pourbaix diagrams (Wahed E.A.M. and Pourbaix M., 1954). Two such diagrams for the secondary and tertiary level anodic corrosion reactions are shown in figure A3 and A4 and can be used to determine the final end product for the secondary corrosion product, which is $Fe(OH)_3$ and the tertiary corrosion product, which is Fe_2O_3, if oxygen is present. It also indicates into what the secondary corrosion product will be transformed as a tertiary end product.

The various possible tertiary level anodic reactions that might take place, to transform the secondary level products, $Fe(OH)_3$, $Fe(OH)_2$ and $FeCO_3$ (figure A3) to Fe_20_3 and Fe_30_4 (figure A4) are as follows.

i) The metastable mineral reactant $Fe(OH)_3$, which only forms if oxygen is present, is transformed in time to stable haematite, δ Fe_2O_3,

$$2Fe(OH)_{3(sol)} \rightarrow \delta\ Fe_2O_{3(sol)} + 3H_20 \quad \ldots\ldots\ldots\ldots \quad (A7)$$

ii) The metastable reactant $Fe(OH)_2$, in the presence of oxygen, may be oxidized to haematite, via magnetite, Fe_3O_4 by the following reactions: formation of Fe_30_4 (Feitknecht, 1959):

$$6Fe(OH)_{2(sol)} + O_2 \rightarrow 2Fe_3O_{4(sol)} + 6H_2O \quad \ldots\ldots\ldots\ldots \quad (A8)$$

and δ Fe_20_3 formation, by further oxidation of Fe_3O_4,

$$2Fe_3O_{4(sol)} + \tfrac{1}{2}\ O_2 \rightarrow 3\ \delta\ Fe_20_{3(sol)} \quad \ldots\ldots\ldots\ldots \quad (A9)$$

The overall reaction is given by the sum of reactions (A8) and (A9).

$$6Fe(OH)_{2(sol)} + {}^3/_2\ O_2 \rightarrow 3\ \delta\ Fe_2O_{3(sol)} + 6H_2O \quad \ldots\ldots\ldots \quad (A10)$$

iii) The reactant $FeCO_3$, may be oxidized to either goethite, FeOOH or to haematite, δ Fe_2O_3 via magnetite, Fe_3O_4 if oxygen is present (Sontheimer, Kölle and Snoeyink, 1981 and Feitknecht, 1959). Goethite is formed by the following reaction:

$$2FeCO_3 + \tfrac{1}{2}\ 0_2 + H_2O \rightarrow 2FeOOH_{(sol)} + 2CO_2 \quad \ldots\ldots\ldots \quad (A11)$$

Magnetite is formed by the reaction with oxygen.

$3FeCO_{3(s)} + ½O_2 \rightarrow Fe_3O_{4(sol)} + 3CO_2$ . . . . (A12)

Magnetite can be converted into haematite if oxygen is present.

$2Fe_3O_{4(sol)} + ½\ O_2 \rightarrow 3\ \delta\ Fe_2O_{3(sol)}$ . . . . (A13)

iv) The reactant Fe^{2+}, may be oxidized directly to magnetite and/or haematite on the anode surface through the following reactions if oxygen and water are present:

$3Fe^{2+} + ½\ 0_2 + 3H_2O \rightarrow Fe_3O_{4(sol)} + 6H^+$ . . . . (A14)

formation of haematite

$2Fe^{2+} + ½\ O_2 + 2H_2O \rightarrow Fe_2O_{3(sol)} + 4H^+$ . . . . (A15)

As illustrated in figure A3 and A4 and the reactions above, it follows that for oxygen concentrations, $0_2 > 1$ mg/ℓ, the stable end products are goethite (FeOOH), or haematite (δFe_2O_3). For extremely low oxygen concentrations the stable end products are likely to be siderite ($FeCO_3$) or magnetite (Fe_3O_4).

From the description of the product formation above it thus follows that compounds that can form above the anode are secondary products like $Fe(OH)_2$, $FeCO_3$ and $Fe(OH)_3$ and tertiary products like, $\delta\ Fe_2O_3$, FeOOH and Fe_3O_4. Deposits formed by secondary products are porous with no effect on the anodic reaction rate. Deposits formed by tertiary products are dense and inert and reduce or terminate the corrosion reaction rate (Stumm 1960; Sontheimer *et al.*, 1981, Kölle and Rosche, 1980) If the rate of formation of secondary products exceeds the rate of formation of tertiary products, tertiary product film will not form, a situation will manifested by either "red water" discharge or "turbercule" formation. "Red water" is evident if the pH ≤ 7, and "turbercules" may appear if the pH ≥ 7,5 (Stumm and Morgan, 1970).

The rate of oxidation of Fe^{2+} to Fe^{3+} in oxygenated water depends on pH and the *partial pressure of dissolved oxygen:*

$$-\ \frac{d[Fe^{2+}]}{dt} = k\,[Fe^{2+}]\ .\ 10^{2pH}\ .\ pO_2$$

$$= +\ \frac{d[Fe_{3+}]}{dt}$$

k = rate constant
pO_2 = partial pressure of dissolved oxygen in Atmospheres
$[Fe^{2+}]$ = Ferrous ion concentration in moles/ℓ

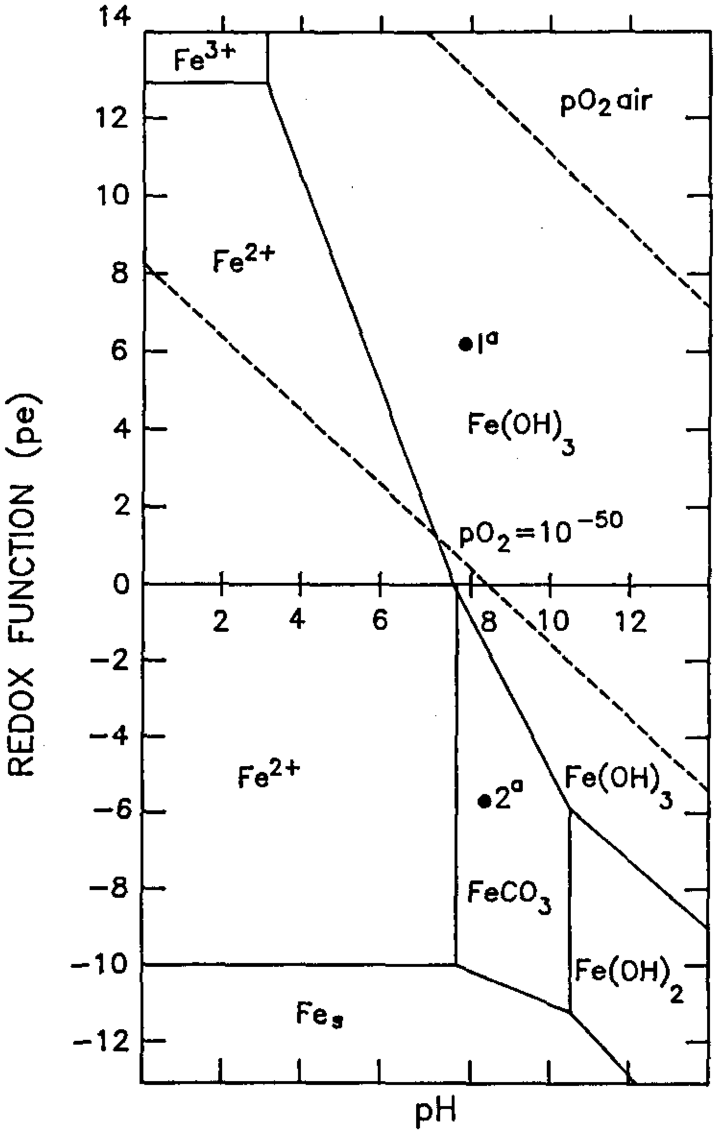

Figure A3 pe – pH diagram for metastable equilibruim of the iron – carbonate – water system; $Fe_T=10^{-5}$ moles/l, $C_T=10^{-3}$ moles/l and temperaure 25° C

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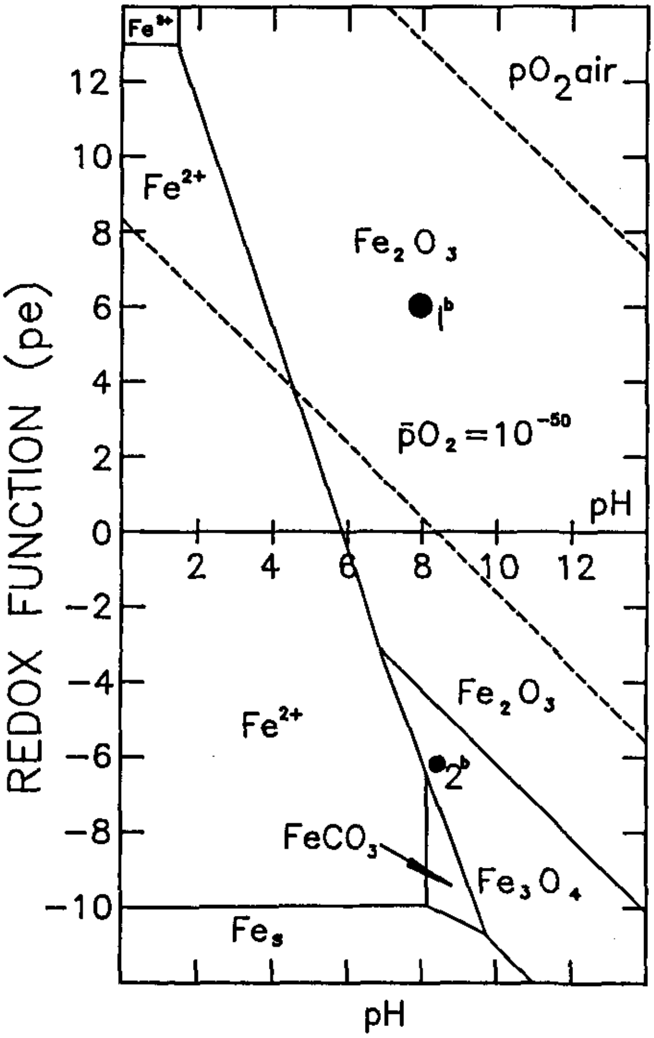

Figure A4 pe – pH diagram of the iron – water – carbonate system; $Fe_T = 10^{-5}$ moles/l $C_T = 10^{-3}$ moles/l and temperature 25° C

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At pH < 7 The rate of oxidation of Fe^{2+} to Fe^{3+} is slow and most of the Fe^{2+} passes through the monolayer into the bulk of the solution. In the bulk of the solution Fe^{2+} is oxidized to Fe^{3+} and the secondary and tertiary products are precipitated in a finely dispersed form that gives rise to "red water".

At pH >7 The rate of oxidation of Fe^{2+} to Fe^{3} is rapid and consequently most of the oxidation occurs in the monolayer. Secondary products precipitate within the monolayer onto the surface as porous deposits in the form of tubercules. Subsequently the secondary products are oxidised to tertiary products but the tubercule formation is not disturbed. These tubercules are porous and do not form an effective seal and corrosion continues.

Passivation cannot be attained via the above mechanisms. The *crux* of the problem lies in the rate of Fe^{2+} formation and this rate is determined by the reactions at the cathode. If the cathodic reaction can be reduced to the extent that Fe^{2+} formation is so slow that tertiary product formation at the anode can take place at the same rate as the secondary product formation, then the tertiary products will form a dense film on the surface.

1.4.2 Cathodic reactions

Oxygen may react as electron acceptor at the anode and the reaction will be:

$$\tfrac{1}{2} 0_2 + 2H^+ + 2e \rightarrow H_20 \quad \text{(A16)}$$

Reactions (A1) and (A16) are two half reactions, the sum of which gives the overall corrosion reaction,

$$Fe_{(s)} + \tfrac{1}{2} 0_2 + H^+ \rightarrow Fe^{2+} + H_20 \quad \text{(A17)}$$

The rate of the overall corrosion reaction is governed by the slower of the two half reactions. The manner in which these two half reactions control corrosion becomes evident by considering pure water that contains carbonate and calcium species.

In pure water the corrosion rate is cathodically controlled by the rate of oxygen supply to the cathode. In such water corrosion protection by oxide film formation is not possible because:

a) If oxygen supply is limited, the cathodic reaction as well as the anodic reactions are slow and consequently the $Fe(OH)_2$ formation will be slow. The formation of iron oxides is even slower so that $Fe(OH)_2$ continuously displaces the oxide from the metal surface and an oxide film has no opportunity to form.

b) If oxygen supply is high, $Fe(OH)_2$ and $Fe(OH)_3$ formation will be so rapid that tertiary products cannot form against the anode surface and "red water" or "tubercule" formation will occur at low and high pH respectively.

In water containing calcium and carbonate species oxygen abstraction of H^+ over the cathode (reaction A16) will cause the pH to rise thereby increasing the CO_3^{2-} concentration. If the $CaCO_3$ solubility product is exceeded, precipitation of $CaCO_3$ takes place over the cathodic area therefore reducing its effective size. If the catholically controlled corrosion rate is reduced sufficiently to allow tertiary oxide film formation on the anode, passivation will go to completion. However, if the rate of $CaCO_3$ precipitation onto the cathode is fast the precipitate will be colloidal or microcrystalline in composition. If the rate is slow, well defined calcite crystals will form. These crystals are porous and permeable and do not slow down the cathodic reaction sufficiently for anodic oxide film formation to occur. For passivation the rate of precipitation onto the cathode surface must be rapid.

1.5 VARIABLES AFFECTING CORROSION AND PASSIVATION

Variables in the bulk liquid that affect the corrosion rate and passivation include,

1.5.1 dissolved oxygen concentration
1.5.2 velocity of flow
1.5.3 calcium and/or carbonate species content and pH in the bulk solution
1.5.4 buffer capacity
1.5.5 presence of certain organic substances and
1.5.6 concentration of chlorides and sulphates

The effects of each of the factors can be described as follows:

1.5.1 Dissolved oxygen concentration

Dissolved oxygen has a dual influence on the corrosion passivation process. Firstly it acts as an electron acceptor at the cathode which increases the rate of corrosion and the rate of abstraction of protons, H^+, from the water adjacent to the cathode. Secondly, it may act as an electron acceptor at the anode allowing formation of passivating oxides at this surface. The abstraction of protons at the cathode causes the pH to rise and this in turn causes an increase in the concentration of CO_3^{2-} and thereby an increase in the rate of $CaCO_3$ precipitation. No information is available as to the limiting effect of oxygen concentration in the bulk solution that will ensure adequate supply to the monolayer.

1.5.2 Velocity of flow

At low flow velocities the oxygen concentration in the monolayer above the cathode and/or the anode becomes limiting in which event the corrosion rate will slow down. The calcium and carbonate species may become limiting thereby slowing down the $CaCO_3$ precipitation rate at the cathodic surface. At higher velocities the corrosion rate and $CaCO_3$ precipitation rate are likely to be higher initially, provided the bulk solution contains sufficient concentrations of calcium carbonate and oxygen species. The higher the precipitation rate, the more microcrystalline and impermeable the $CaCO_3$ precipitant over the cathodes will be, and the greater the possibility for eventual passivation via anode oxide protection. In contrast, the lower the velocity, the more macrocrystalline and permeable the $CaCO_3$ precipitant over the cathode will be, therefore reducing the possibility of passivation. It is also important to note that super saturation of the bulk solution with respect to calcium carbonate does not guarantee passivation, neither does under saturation necessarily enhance corrosion. The passivation potential of the two samples with about the same chemical composition were investigated by Miller and Loewenthal (1982). The pH of the samples were 7 and 8,1 and CCPP values 40,0 and 2,0 respectively. Passivation was attained after about 30 days at pH 7 and 40 days at pH 8,1 at a flow rate of 17 cm/s but not at a flow rate of 5cm/s. Water velocity can thus determine if passivation or continuous corrosion could occur.

1.5.3 Calcium and carbonate species concentration in the bulk solution

a) At the cathode: At high concentrations of calcium and carbonate species, with cathodic abstraction of H^+, the monolayer will be super saturated and microcrystalline impermeable calcium carbonate scale will form.

b) At the anode: Firstly dissolved carbonate species reduce the corrosion stimulating effect of chloride and sulphate anions, Evans, (1981), this aspect is discussed in detail in paragraph 1.5.6.
Secondly, HCO_3^- and CO_3^{2-} species act as a reservoir of OH^- species that is necessary for the formation of $Fe(OH)_2$, $Fe(OH)_2$, Fe_3O_4 and Fe_20_3 at the anode surface. If the total carbonate species concentration, C_T, is high and if the pH is in the region of high buffering capacity, a reservoir of OH^- can be maintained at the anode surface without significant pH changes even where the OH^- concentration is relatively low, i.e. pH ≤ 8. In this case the formation of secondary products [$Fe(OH)_2$, $Fe(OH)_3$] will be slow and tertiary product formation can take place (passivation) .
Thirdly, a high carbonate species concentration increases the formation of siderite ($FeCO_3$) that can seal the cracks in the tertiary anodic ferric oxide film or can, with time, alter to form a protective calcium carbonate or iron oxide, Fe_30_4, film. Stumm, (1960) suggests the following reaction

$$FeCO_{3(sol)} + Ca^{2+} \rightarrow CaCO_{3(sol)} + Fe^{2+}$$

and Sontheimer *et al.*, (1981) suggest the reaction

$$3FeCO_{3(sol)} + 3H_20 + \tfrac{1}{2}0_2 \rightarrow Fe_3O_{4(sol)} + 3H^+ + 3HCO_3^-.$$

1.5.4 Buffer capacity

Stumm, (1960) found that if the pH next to the cathode differs appreciably from that over the anode, the corrosion pattern is one consisting of a relatively small number of large cathodic and anodic regions. If the pH difference is small, the pattern is one of a relatively large number of small cathodic and anodic regions. The latter pattern,

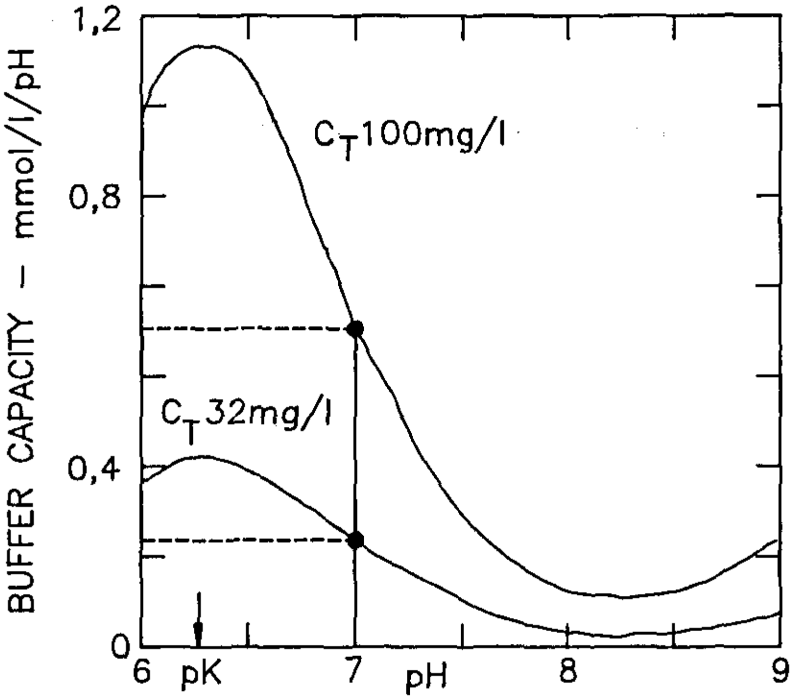

Figure A5 Effect of total carbonate concentration and pH on the buffer capcity of water

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Stumm concluded, has a higher likelihood to give rise to passivation. Stumm further comments that the magnitude of the difference in pH between the cathode and anode is affected significantly by the buffer capacity, ß, in the bulk solution. Buffer capacity, ß, is defined as the moles/ℓ of strong base, required to effect a unit change in pH. If the buffer capacity is relatively high, the pH difference will be relatively small and *vice versa*.

The buffer capacity in water supplies is determined by the total carbonate species concentration (C_T) and the pH. To illustrate this, see Figure A5 in which the buffer capacity versus the pH of two waters having respective total carbonate species concentration, C_T, of 100 and 32 mg/ℓ as $CaCO_3$ is illustrated. As can be seen the buffer capacity at pH 7 is higher than at pH 8, therefore the pH differences between the anode and cathode is smaller at pH 7 than at pH 8. Thus passivation has a higher likelihood to occur at pH 7 than at pH 8.

1.5.5 Influence of certain organic material on the nature of $CaCO_3$ precipitate

From investigations done by Larson (1975), Campbell (1980), Sontheimer *et al.* (1981), Ruddic (1981) Campbell and Turner (1983) it appear that the presence of certain humic and other organic substances (as yet unidentified) lead to an eggshell like $CaCO_3$ precipitate on the cathode which reduces the corrosion current both by decreasing the cathodic area and by polarising the cathode. Sontheimer *et al.* suggest that corrosion protection is attained when the concentration of humic substances exceeds about 0,6 mg/ℓ as dissolved organic carbon.

1.5.6 Chloride and sulphate concentrations

There is general acceptance that chloride and sulphate ions stimulate the rate of corrosion and inhibit passivation. Evans (1981) explains the behaviour as follows: chloride and sulphate ions are adsorbed onto the anodic surface thereby displacing water, oxygen and hydroxide species, any Fe^{2+} ion released at the anode disperses into the bulk solution where secondary and tertiary reactions can occur, giving rise to a finely suspended colloidal form of iron oxides, δFe_2O_3, FeOOH or Fe_3O_4. As a consequence no oxide film forms on the anode surface and no passivation is achieved. Sulphate species can also give rise to biologically mediated corrosion in anaerobic environments like tubercules. A bacterial species known as Desulfovibrio desulfuricans oxidises solid iron to the ferrous ion (Fe^{2+}) and reduces sulphate to sulphide. The ferrous sulphide and hydroxide ions precipitate as FeS (pyrite) and $Fe(OH)_2$ none of which forms a passivating film (Kölle and Rosch, 1980). Biologically mediated corrosion appears to be a secondary effect in a corrosive situation whereby turbercules (pH >7,0) exists.

The Water Research Centre (1981) in the United Kingdom suggested that water containing more than 50 mg/ℓ of either chloride or sulphate should be regarded as potentially corrosive. However, as early as 1927 it was observed that the presence of carbonic species (HCO_3^- and CO_3^{2-}) reduces the corrosive effect of chlorides and sulphates (Evans 1981). This effect arises from the competitive adsorption of the carbonate species onto anodic surfaces, displacing some of the Cl^- and SO_4^{2-} ions. Larson (1971) makes the statement that the passivating action of water saturated with calcium carbonate "is decreased by increasing proportions of chloride and sulphate salts above a ratio of 0,1 to 0,2 with respect to alkalinity". A number of authors appear to have accepted the upper limiting ratio of ($Cl^- + SO_4^{2-}$)/alkalinity to be $\leq 0,2$. In South Africa, the City of Johannesburg it was shown that during the period 1940 - 1980 the ratio increased from 0,4 to 3,0 and in the same period the number of repairs to water mains increased about eighteen fold, probably caused by sulphate reducing bacteria (Osborn, 1984). Another contributing factor could also be related to the age, forty to sixty years, of these mild steel pipes. In conclusion it is likely that most inland waters of South Africa with its high chloride and sulphate concentrations are highly corrosive.

1.5.7 Conductivity

The effect of conductivity has largely been ignored in all corrosion studies with the aim to obtain a reliable corrosion index. (Singley 1981). A Stone *et al.* 1987, however, investigated the effect of increasing chloride, sulphate and bicarbonate concentrations on the corrosion rates of copper and zinc by making use of the linear polarization technique. In all cases the corrosion rate increased due to in increase of conductivity caused by an increase in concentration of the above mentioned chemical species.

2. TYPES OF CORROSION

2.1 UNIFORM CORROSION

Uniform corrosion prevails if the location of oxidation and reduction sites constantly shift. Uniform corrosion is therefore favoured by a clean metal surface and an ample supply of cathodic reactant. Thus in acidic solutions, where oxide films are absent and the concentration of hydrogen ions is high, steel corrodes uniformly. It also manifests itself in the formation of covering layers of corrosion products (Hargarter, 1980).

2.2 LOCALISED CORROSION

2.2.1 Pitting

If an oxidation site becomes small, fixed, and surrounded by a much larger reduction area, then localised corrosion such as pitting can result. An oxidation site becomes small because of the local breakdown of a protective film or a break in a deposit on the metal. (Swigley *et al.*, 1985). Exposed metal in the pit area is anodic, and cathodic in the surrounding area (Behnke, 1987). Pit corrosion can also be promoted by the accumulation of chloride and hydrogen ions in a pit underneath a precipitated layer on the metal (Sato, 1989). On stainless steel, pitting may also be caused by bromides, hydrogen sulphide and sulphur dioxide. Pitting occurs underneath deposits as a result of varying aeration, and is often found at the material/water/atmosphere phase

TABLE A1: CALVANIC SERIES OF SELECTED METALS AND ALLOYS IN SEAWATER[1]

ANODIC, ACTIVE (Read downwards)(least resistant to corrosion)	Manganese bronze
Magnesium	Naval base
Magnesium alloys	Nickel (active)
Zinc	Inconel - 75% Ni, 16% Gr, 7% Fe (active)
Aluminium 52SH	Yellow brass
Aluminium 4S	Aluminium bronze
Aluminium 3S	Res brass
Aluminium 2S	Copper
Aluminium 53S - T	Silicon bronze
Alclad	Ambrac - 5% Zn, 20% Ni, 75% Cu
Cadmium	70% Cu, 30% Ni
Aluminium 17S - T	Comp. G bronze - 88% CU, 2% Zn, 10% Sn
Aluminium 24S - T	Comp. M Bronze - 88% Cu, 4% Zn, 6,5% Sn, 1,5% Pb
Mild steel	Nickel (passive)
Wrought iron	Inconel - 75% Ni, 16% Cr, 9% Fe (passive)
Gray and uctile cast iron	Monel - 70% Ni, 30% Cu
Ni-resit	18 - 8 stainless steel, type 304 (passive)
13% Cr stainless steel, type 410(active)	18 - 8, 3% Mo stainless steel, type 316 (passive)
50-50 lead-tin solder	Titanium
18-8 stainless steel, type 304(active)	Silver
18-8 3% stainless steel, type 316(active)	Graphite
Lead	Gold
Tin	Platinum
Muntz metal	CATHODIC, NOBLE (Read upwards) (most resistant to corrosion)

---

[1] In a galvanic cell of two dissimilar metals, the more active will perform as the anode and be corroded, while the more noble metal will perform as the cathode and be protected

boundary. Varying levels of aeration intensifies pit corrosion, and pitting is often observed in pipe lines during shutdowns.

2.2.2 Crevice corrosion

Crevice corrosion is attributable to corrosion cells formed by differences in concentration in the corrosive medium, particularly as a result of an oxygen deficiency inside the crevice. Crevices are found between metal sections, or a metal and a non-metal joint. In pipe systems the flange joints and also notches in welds may form crevices. Crevice corrosion also occurs underneath deposits such as welding beads or debris. This type of corrosion mainly occurs on materials which can be passivated (Hargarter, 1980).

2.3 GALVANIC CORROSION (CONTACT CORROSION)

If two different types of metals are in contact with each other in the presence of water containing dissolved salts, a galvanic couple can form in which case the metal acting as the anode, will corrode. Table A1 shows the galvanic series of selected metals and alloys in seawater (Behnke, 1987). When any two of the metals shown in the series are connected with the electrolyte and a return current path to form a galvanic cell, the metal nearer the top of the series will form the anode and will corrode, the metal nearer the bottom of the series becomes the cathode, and thus remains protected. The metals on the cathodic end of the series are said to be more noble than those on the anodic end. Calvanic corrosion can occur where several different metals and alloys are used, for instance in the construction of a large valve.

2.4 SELECTIVE CORROSION

Selective corrosion is a type of corrosion in which a specific metal from an alloy is dissolved out. Yellow brass, which consists of about 30 percent zinc and 70 percent copper is a good example in which selective corrosion can take place. In certain wet environments, zinc may be lost from the brass, leaving a porous copper mass of greatly reduced strength. This effect is termed dezincification (Behnke, 1987).

2.5 CAVITATION CORROSION

Cavitation corrosion is caused by mechanical attack on the metal surface resulting from the collapse of water vapour bubbles in fast flowing water. This takes place in zones in which the pressure of the water is reduced rapidly, as a result of exceeding the critical water flow rate, to such an extent that water vapour is formed. The violent blows resulting from the hammer like collapses of the vapour bubbles destroy not only the top layers, but also the metal itself. The mechanically activated surface is then additionally corroded by the chemical action of the water (Hargarter 1980).

2.6 VIBRATION CORROSION CRACKING

This is corrosion caused by cracks formed by low frequency stress cycles and small loads, so called low cycle corrosion fatigue, in which cracks are usually relatively small but numerous. Individual cracks can occur at high frequencies and high stresses (Hargarter 1980).

2.7 CONCENTRATION CELLS

Concentration cells are localised occurrences of corrosion that often develop at crevices in metal units owning to the uneven diffusion of oxygen. The oxygen content inside the crevice may be very low compared to that in the environment just outside the crevice. In this case, metal at the site of low oxygen concentration will become anodic, and corrosion will occur within the crevice (Behnke, 1987).

2.8 IMPINGEMENT CORROSION ATTACK

Many metals under normal conditions form protective surfaces as a result of the manufacturing process (Behnke, 1987). An extremely forceful stream of water may break through this protective surface and cause corrosion to develop.

2.9 BACTERIOLOGICAL CORROSION

Byproducts of sulphate reducing bacteria cause bacteriological corrosion (Behnke, 1987). These bacteria live in environments where there is little or no oxygen and where the pH is near neutral. Their life processes give off sulphides by the following reaction (Williams, 1984).

$$8H^+ + 8e^- + SO_4^{2-} \rightarrow S^{2-} + 4H_2O$$

Sulphides are excellent electrolytes and for this reason aggressive to metal surfaces.

2.10 SOIL CORROSION

Most soil corrosion of metals occurs in soil of high electrical conductivity (Behnke, 1987). Non-uniformity of the soil, chemical contamination or the presence of areas of high and low oxygen content may increase the problem. Sometimes low resistivity soils act in combination with sulphate reducing bacteria to create extremely aggressive conditions. Table A2 lists some typical soil corrosion cells that result from variances in electrolyte concentration along a metal surface.

The pH of the soil may be significant. Acid soils, with pH below 5,0, are generally aggressive. A neutral pH of 6,5 to 7,5 does not indicate corrosive conditions, unless sulphate reducing bacteria are involved. High pH soils are usually not aggressive to ferrous metals, owing to their alkalinity, however, they are usually high in soil salts, that will cause low soil resistivities and make such soils good electrolytes. Moisture is generally a requirement for soil corrosion, because dry soils make poor electrolytes. Very dry soils seldom cause corrosion problems.

TABLE A2: TYPICAL SOIL CORROSION CELLS RESULTING FROM NON-UNIFORM ELECTROLYTE CONDITIONS.

ANODIC AREA	CATHODIC AREA
Low oxygen	Higher oxygen
Low resistivity	Higher resistivity
Sulphate reducing bacteria	No sulphate reducing bacteria
Water saturated soil	Drier soil
Organic contamination (dead vegetation, leaves, refuse)	Clean soil
Contact with highly conductive material (cinders, coal salts)	Clean soil

2.11 ATMOSPHERIC CORROSION

Atmospheric corrosion requires atmospheric humidity and an oxidising agent, usually oxygen (Behnke, 1987). Most water treatment plants have areas where materials are constantly exposed to very humid conditions. The result is rusting of iron or steel. In these environments, chlorine, fluorine, iodine and bromine are extremely active oxidising agents. Atmospheric corrosion may tend to cause an uniform corrosion attack. Oxidising agents (acids, chlorine, etc) dissolve the corrosion product layer, and oxidation continues.

3 INHIBITORS

By definition a corrosion inhibitor is a substance which, when introduced into an environment in relatively small concentrations, will drastically decrease the corrosion rate of a relevant construction material.

The effectiveness of an inhibitor (inh) can be calculated with the following equation.

$$\text{Eff} = \frac{\text{corr rate without inh. - corr rate with inh.}}{\text{corr rate without inh.}} \text{ X } 100\%$$

Effectiveness is a function of the type of metal, type of environment, inhibitor concentration and system conditions like temperature and turbulence (Introduction to Corrosion, 1993).

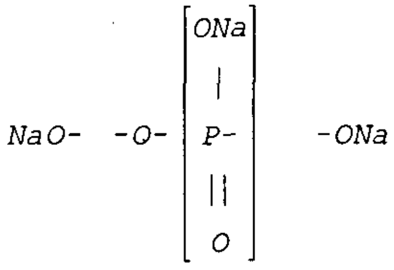
3.1 TYPES OF INHIBITORS

Organic inhibitors with functional groups like -COOH, -OH, $-NH_2$, -SH, -CN, $-NO_2$, NCS, -CHO and SO_3H that have a sufficiently large dipole moment (White, 1986).

Polycarboxylic acids are usually used in combination with other chemicals e.g. polymalic acid is a particularly effective corrosion inhibitor when used in combination with zinc.

Nitrogen containing compounds include anions, pyridine bases and others. Their effectiveness depends on their adsorption or complexing properties, or both, and their application has been restricted chiefly to metal pickling.

Polyphosphates used for corrosion control are linear polymers with the following general formula. Chains are formed between two or more molecules.



$$NaO- \quad -O- \left[\begin{matrix} ONa \\ | \\ P- \\ \| \\ O \end{matrix}\right] \quad -ONa$$

For optimum efficiency, the chain must consist of between 14 and 16 molecules. The low dosage levels of 15 to 20 mg/l make their use very economical (Harris and Marshall, 1980). Polyphosphates also act as scale inhibitors because they retard the precipitation of supersaturated solutions of $CaCO_3$. A disadvantage of inorganic polyphosphates is their relatively rapid degradation in water and reversion to orthophosphates.

Phosphonates, in phosphonate compounds, phosphor is bonded in a C-P linkage that results in stable compounds that are far more resistant to hydrolysis at elevated temperatures and extremes of pH. They are not effective when used alone, but in combination with other inhibitors such as zinc, chromate, polyphosphates, and silicates, they give good protection. Average dosage is 1 mg/ℓ as P_2O_5.

Zinc salts, inhibitive action is due to the precipitation of $Zn(OH)_2$ on the cathodic areas at elevated pH. It is always used with other cathodic polarizers in order to give a more durable film.

Ferrous sulphate is an effective inhibitor of copper alloys and will not be discussed further.

Chromates are effective passivating inhibitors but because of their toxicity will not be discussed further.

Molybdates in the form of sodium molybdate are useful inhibitors where there is local attack because insoluble MoO_2 precipitate in crevices (Wanklyn, 1981).

Chelating compounds as corrosion inhibitors are organic molecules with at least two polar functional groups, and are capable of ring closure with a metal cation (McCafferty, 1978).

Multi component inhibitors frequently provide better inhibition than single inhibitors. Harris and Marshall (1980), have illustrated a method for the selection of inhibitors for various applications based upon the Ryzner Stability Index, and the potential or existing problem (See Figure A6).

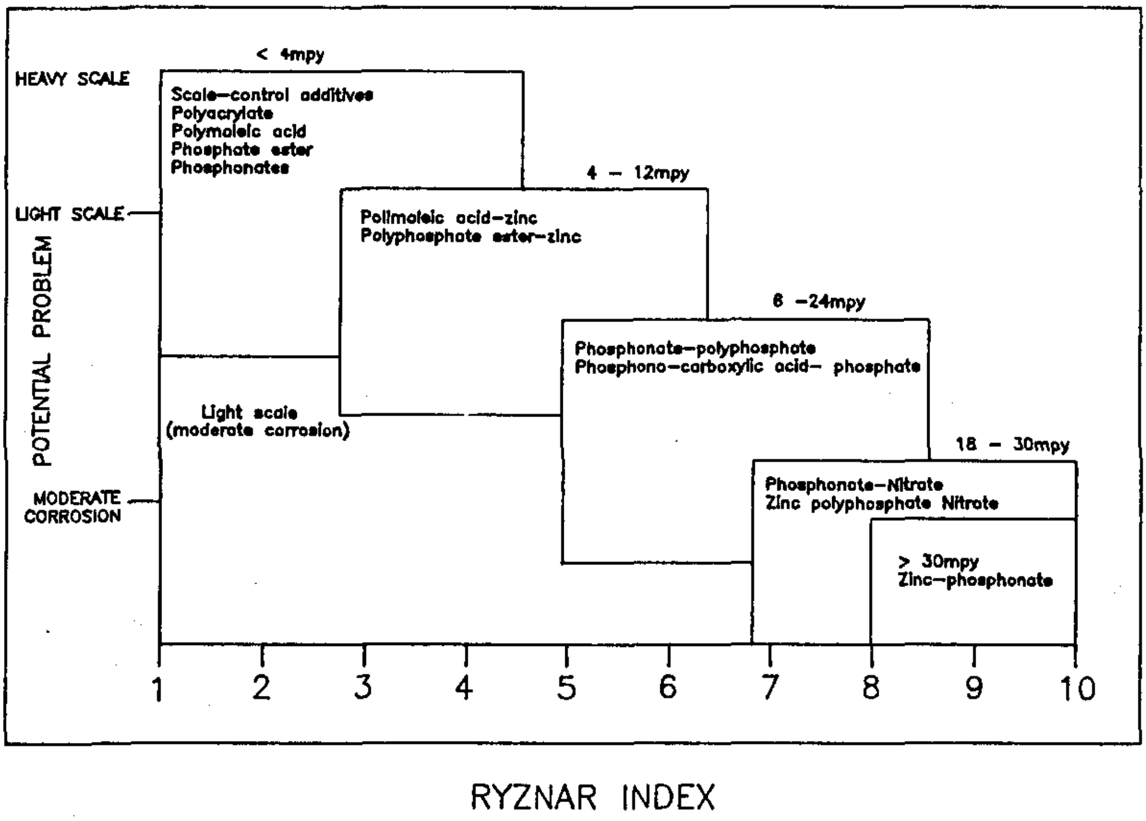


Figure A6 Treatment to stop or prevent corrossion as determimnied by the Ryznar stability index

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3.2 PARAMETERS TO BE CONSIDERED IN THE APPLICATION OF INHIBITORS (White, 1986).

The parameters to be considered before inhibitors are used, include the following:

(a) The compatibility of the inhibitor molecule with the system.

(b) The density of the inhibitor, which is important for proper mixing.

(c) Desirable effective solubility, i.e. some solubility is required for mixing in the system, although hydrophobicity is a prerequisite to ensure adsorption onto the corroding surface.

(d) Surface active characteristics i.e. the inhibitor must disperse easily and be primarily hydrophobic in character, but not so highly active as to form soap micelles and therefore foam.

(e) The formation of sludges or precipitates due to the use of corrosion inhibitors must be prevented because it will reduce the concentration thereof and consequently its effectiveness.

(f) The temperature of the system, many organic inhibitors exhibit thermal degradation.

(g) The pH of the solution.

(h) The diffusion rate through the boundary layer.

(i) Undesirable ecological effects, like the toxicity of chromates.

(j) Costs, studies of the most economical chemicals are imperative.

3.3 VARIOUS COMPONENTS OF A WATER SYSTEM THAT MUST BE CONSIDERED

Metal cations:- Divalent cations can precipitate inhibitors such as phosphate and silicates at high concentrations.

Alkali (OH^-):- Steel can be passivated but zinc, aluminium and lead corrode considerably at a pH above 9.

Chloride (Cl^-):- Chloride ions are strongly adsorbed by steel, making it difficult to passivate and the amount of inhibitor required rises in proportion to the chloride concentration.

Sulphate (SO_4^{2-}):- Although not as severe in effect as chloride, sulphates can depassivate a surface by precipitation and cause certain inhibitors to coagulate.

Sulphides(SO_3^{2-}):-	Oxidising inhibitors are reduced by sulphide, therefore requiring high inhibitor concentrations for effectiveness.
Oxygen:-	Organic inhibitors are generally not effective against oxygen - based corrosion unless passivating groups such as benzoates or sulphonates are present. If organic inhibitors are used the dissolved oxygen concentration must be reduced to less than 1mg/l to obtained steel passivation.
Acids:-	Passivating inhibitors cannot be used in high hydrogen ion concentrations.
Bicarbonate:-	In hard water, deposited mineral scales will impede corrosion but, in soft water, excess carbon dioxide will produce acidic conditions requiring the addition of inhibitors.

3.4 INHIBITING EFFECT OF SILICATE, POLYELECTROLYTE, CHLORINE AND MONOCHLORAMINE

3.4.1 Silicate

Sodium silicate as a corrosion inhibitor was investigated because it is used by Rand Water as a coagulant aid in the water purification process. Soluble silicate with varying ratios of sodium oxide (Na_2O) and silica is produced by fusing sodium carbonate (Na_2CO_3) with silica sand (SiO_2) at high temperature and pressure. (Tresh, 1922 and Lehrman 1952).

As a dry chemical, called water glass, with chemical composition of Na_2SiO_3, $Na_6Si_2O_7$ or $Na_2Si_3O_7$ and with various amounts of hydrated water, it is used in pot feeders on hot water systems. As solubles with $Na_2O : SiO_2$ of 1:2 it is used in water with pH ≤ 7 and with $Na_2O : SiO_2$ of 3:3 is recommended for water of pH greater than 7. The sodium silicate used by Rand Water has the latter ratio and is purchased as a solution containing 29% silicate as SiO_2. Silicates can act as a cathodic inhibitor in the presence of oxygen, forming a protective gel over the surface, and are specially useful in badly corroded and turberculated pipes. Initial dosage is 8 - 16 mg/ℓ as SiO_2 (Ainsworth, 1980 and Benjamin, 1990). A modern study conducted by Labodny-Sarc, and Kastelan, (1981) confirmed the anodic character of sodium silicate, in which case it must react with dissolved metal.

The rate of dissolution of steel, as a function of the alkali concentration, varies according to the following law. When the alkali is added, the true corrosion rate increases to a maximum after which it decreases. Sodium silicate is a non oxidising precipitation inhibitor that will produce anions with different adsorption characteristics (White, 1986). These anions are formed as follows:

Sodium silicate, that is alkaline in nature, can be activated in water containing carbon dioxide by way of the following reactions.

$CO_2 + H_2 \leftrightarrow H_2CO_3$ . . . . (A18)

$Na_2O.SiO_2 + H_2CO_3 \rightarrow SiO_2.H_2O + Na_2O + Na_2CO_3$ . . . . (A19)

and the product $Si0_2.H_2O$, silicic acid can polymerise forming a gell that can act as a protective layer against corrosion. If the polymerisation process does not proceed too far, strong negative anionic polyelectrolytes with the general formula, $2nH^+(SiO_3^{-2})_n$, forms that can act as adsorbents for corrosion products like (Fe^{2+}). The problem with silicates as inhibitors is their slow protective development and pH dependability making them unsuitable in the environment with pH <6.

In more general terms it can be said that silicate forms continues amorphous silica protective scale in mild steel pipelines that could only form after corrosion products like $Fe(OH)_2$, $Fe(OH)_3$ and Fe_2O_3 had formed an anchoring scale (Economic and Engineering Services, 1989). The silicate protective layer forms a double layer with metal oxides and carbonates on the metal surface with the metal oxides and carbonates in a layer between the metal surface and the silicate layer.

The silicate layers are thin (does not build up to thick layers) and will get thinner if treatment is stopped. For new pipelines high dosages are required as pretreatment. In old pipelines old accumulated corrosion products will be removed by high silicate dosages.

3.4.2 Polyelectrolyte coagulants

The polyelectrolyte that was tested for its corrosion inhibition effects is normally applied by Rand Water as a coagulant in the water purification process. Its chemical composition is that of a polyamine and it can be classified as a adsorbed layer former which show polar characteristics. It can be adsorbed on metal surfaces by means of columbic forces whereby it will interfere with corrosion reactions in such a way that corrosion rates will drastically be reduced (Introduction to Corrosion 1993). It is effective for protection of metals in acid media where the hydrogen cathodic reaction is dominant. Adsorbed layer formers are also available for neutral pH solutions although their use is not as widespread. Examples are organic compounds containing nitrogen, like fatty amines being used for carbon steel.

3.4.3 Chlorine and monochloroamine

Free residual chlorine in excess of 0,5 mg/ℓ in potable water accelerates corrosion of mild steel probably because of the formation of chloride ions, while chloramine act more as a corrosion inhibitor (Economic and Engineering Services, 1989).

4. MEASURING CORROSION RATES

Because of the electrochemical nature of most corrosion processes,electrochemical techniques can be used to measure corrosion rates in specific environments (Rohrback, Cosasco Systems, Inc. 1991).

4.1 BASIC ELECTROCHEMICAL PRINCIPLES

Metal atoms are oxidised to form positive ions (cations) while other chemical species (e.g. O_2, H_2O or other cations) are reduced. This results in a flow of electrons from one site on the metal surface to another. Consider the corrosion of iron in hydrochloric acid as depicted in Figure A7 (Page A.27). The overall reaction is described by equation:

$$Fe + 2HC\ell \rightarrow FeC\ell + H_2 \uparrow \quad \text{(A20)}$$

This reaction can be considered as the sum of two different reactions occurring at different sites on the metal surface.

$$Fe \rightarrow Fe^{2+} + 2e \text{ (oxidation)} \quad \text{(A21)}$$

$$2H^+ + 2e \rightarrow H_2 \text{ (Reduction)} \quad \text{(A22)}$$

A site where oxidation occurs is defined as an anode and one where reduction takes place as a cathode. The anodic and cathodic areas together form a corrosion cell and the reactions at each site are a half cell. The hydrochloric acid in this reaction is the electrolyte, a fluid containing ions which migrate in an electric field. The electron flow occurs in the metal and flow from the anode to the cathode area on the metal surface. A corrosion cell therefore consist of four parts, namely the anode area, cathode area, electrolyte and a metal conductor. The current which flows in the corrosion cell per unit area is referred to as the Corrosion Current Density (I_{corr}). Since I_{corr} is a measure of current (electron) flow per unit area per unit time, it is directly related to units of metal loss per time, which is how corrosion rate is expressed (micron per year of metal thickness reduction).

Each half cell reaction has a characteristic potential, called the Redox Potential which is the potential of the half cell reaction when it is at equilibrium in a solution of its own ions compared to the potential of a standard hydrogen reference electrode (which has a arbitrarily established potential of 0 volts).

To be in equilibrium means that the rate at which iron in the half cell of Figure A7 (Page A27) is reduced, is equal to the rate that it is oxidised:

Fe → Fe^{2+} + $2e^-$ (oxidation) . . . . (A23)

Fe^{2+} + $2e^-$ → Fe (reduction) . . . . (A24)

It can be demonstrated that each of these reactions has a potential current relationship which can be drawn as a straight line on a semi log graph, as shown in Figure A8 (Page A.27). The point where these two lines cross is where equilibrium exists and is by definition the redox potential of the half cell. The redox potentials of commonly encountered metals are shown in Table A3 (Page A26). The more negative a metal's redox potential, the more reactive it is. So it can be seen that the redox potential of the iron half cell is -0,44 volts.

In order for corrosion to occur there must also be a cathodic reaction. A list of more common cathodic reactions and their redox potentials are presented in Table A4. A graph similar to that in Figure A8 can be drawn for each cathodic reaction in the same way as for the anodic reactions, and at equilibrium the oxidation and reduction reactions proceed at the same rate. Superimposing the graph in Figure A8 and the potential curves for the hydrogen half cell give a polarisation diagram of the complete corrosion cell as shown in Figure A9. Since the two half cells are connected through metal, the two half cells must be at the same potential that occur where the iron oxidation and hydrogen reduction curves cross. This point is defined as the Corrosion Potential, or E_{corr} of the cell and its corresponding current flow through the cell is the corrosion current, or I_{corr}. The Tafel Slope, used in electrochemical measurement techniques, is the slope of the straight line for the anodic or cathodic reaction shown in Figure A10 (Page A.28).

4.2 TAFEL PLOT

In this technique the potential of the working electrode is slowly scanned from approximately -250 mV to +250 mV with respect to the corrosion potential (Scheers 1989).

The principle of this method becomes evident from Figure A10 (Page A.28) in which the potential relative to E_{corr} versus the logarithm of the current density are shown. It must be kept in mind that in a polarisation curve the measured current is the absolute difference between the oxidation current and the reduction current.

Near the corrosion potential (i.e. near the intersection of the oxidation and reduction curves) this subtraction is significant and this accounts for the deviation of the observed curve from the theoretical (dashed line).

In figure A10 the intersection of the extrapolated linear parts of the anodic and cathodic plots gives the corresponding E_{corr} and I_{corr} values. E_{corr} being the corrosion potential and I_{corr} the corresponding corrosion current density.

TABEL A3: REDOX POTENTIALS OF METALS

METAL		REDOX POTENTIAL (VOLTS)
	Active end	
Potassium	$K \leftrightarrow K^+ + e^-$	-2,92
Magnesium	$Mg \leftrightarrow Mg^{+2} + 2e^-$	-2,38
Aluminium	$Al \leftrightarrow Al^{+3} + 3e^-$	-1,66
Zinc	$Zn \leftrightarrow Zn^{+2} + 2e^-$	-0,76
Chromium	$Cr \leftrightarrow Cr^{+3} + 3e^-$	-0,71
Iron	$Fe \leftrightarrow Fe^{+2} + 2e^-$	-0,44
Nickel	$Ni \leftrightarrow Ni^{+2} + 2e^-$	-0,23
Hydrogen	$2H^+ + 2e^- \leftrightarrow H_2$	0,00 Reference
Copper	$Cu \leftrightarrow Cu^{+2} + 2e^-$	+0,34
Silver	$Ag \leftrightarrow Ag^+ + e^-$	+0,80
Platinum	$P+ \leftrightarrow P+^{+2} + 2e^-$	+1,20
Gold	$Au \leftrightarrow Au^{+3} + 3e^-$	+1,42
	Noble or Passive End	

TABLE A4 REDOX POTENTIAL OF CATHODIC REACTIONS

REACTION		REDOX POTENTIAL (VOLTS)
Hydrogen Ion reduction	$2H^+ + 2e^- \leftrightarrow H_2$	0,00
Oxygen reduction in acid solutions	$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	+1,23
Oxygen reduction in base or neutral solutions	$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-$	+0,40
Metal Ion reduction	$Fe^{+3} + e^- \leftrightarrow Fe^{+2}$	+0,77
Metal Deposition	$Cu^{+2} + 2e^- \leftrightarrow Cu$	+0,34

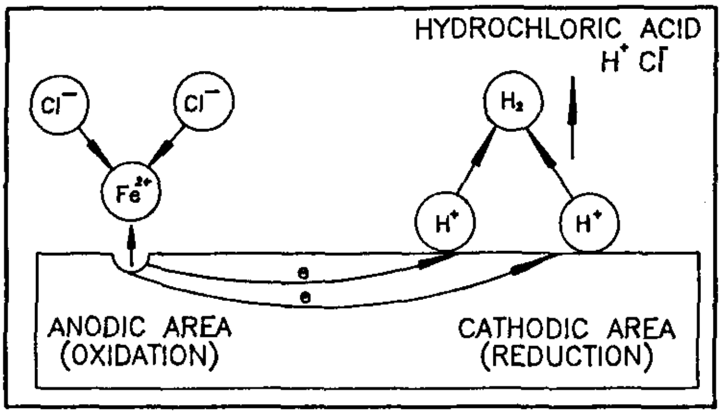

FIGURE A7 DIAGRAM OF OXIDATION AND REDUCTION PROCESSES IN A HYDROCHLORIC ACID/IRON CORROSION CELL

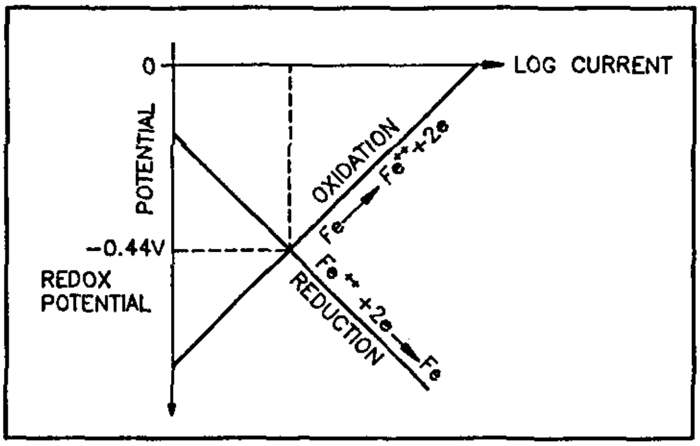

FIGURE A8 POTENTIAL–CURRENT CURVES OF IRON OXIDATION AND REDUCTION REACTIONS

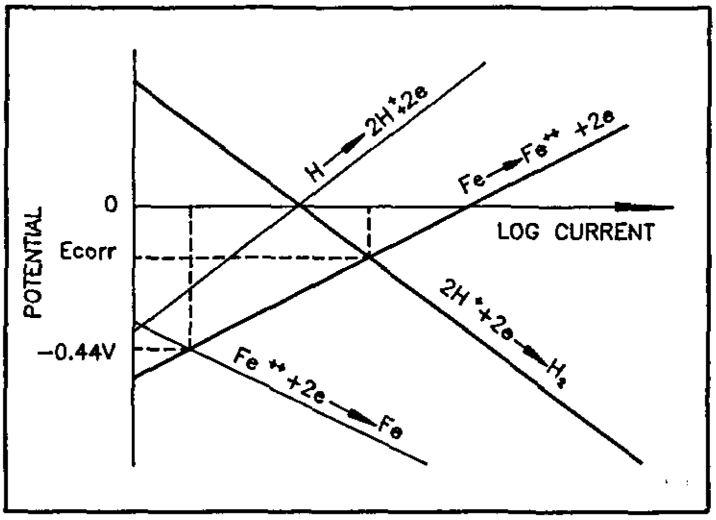

FIGURE A9 POLARIZATION CURVES FOR IRON HCl CORROSION

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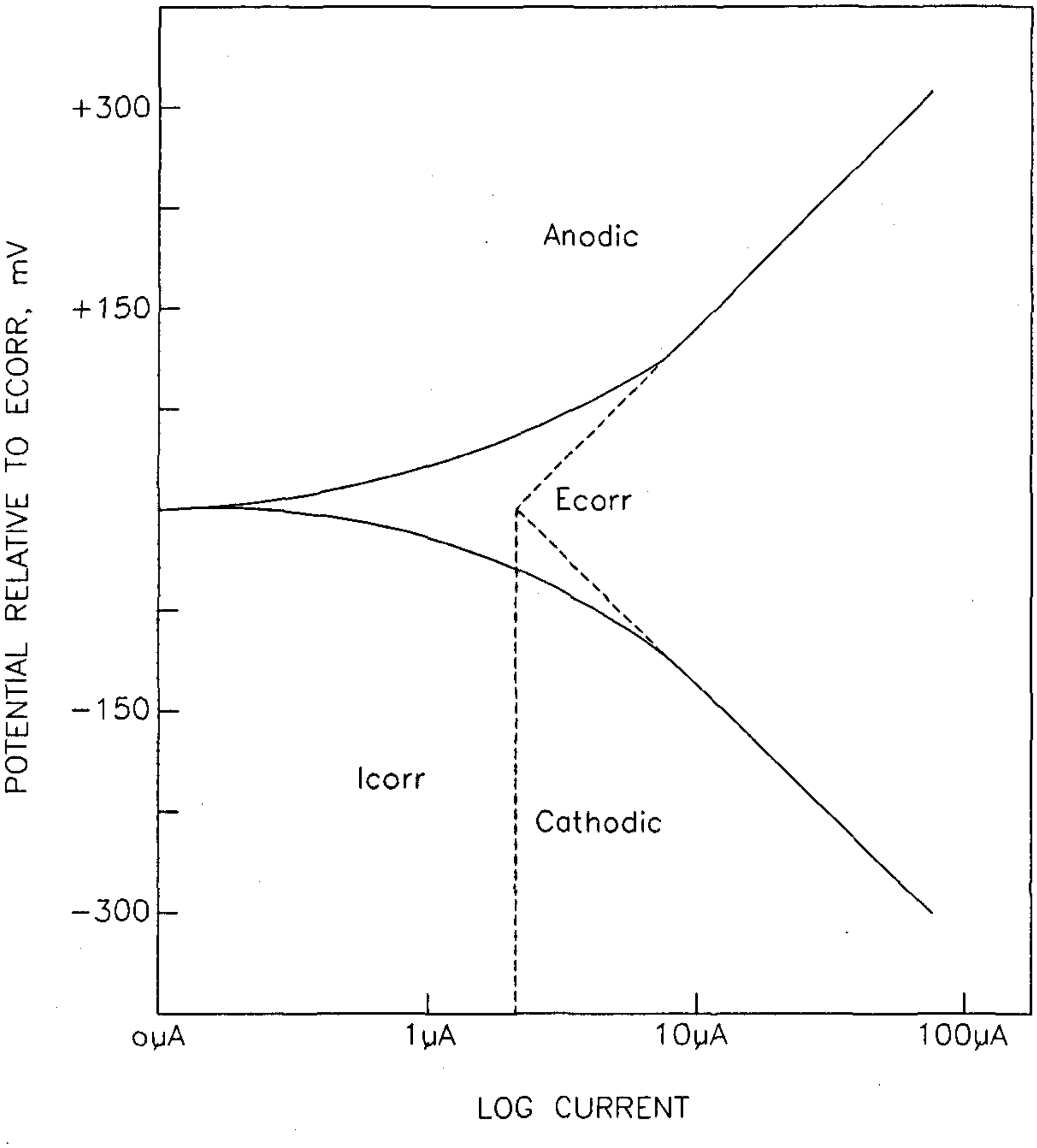

Figure A10 Tafel plot produced from experimental readings

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I_{corr} can be used to determine the corrosion rate of a metal by means of the equation.

$$\text{Corrosion rate } (\mu m/y) = \frac{0.13\, I_{corr}\,(E)}{d}$$

Where

I_{corr} = corrosion current density, $\mu A/cm^2$

E = equivalent weight of the corroding species in gram(g)

d = density of the corroding species, g/cm^3

(Publication of the National Association of Corrosion Engineer, 1972).

This equation is based on Farraday's law stating that the mass of a metal that will dissolve during an electrochemical reaction, is directly proportional to the current flowing through the metal.

$$M \propto I$$

M = mass of metal dissolved

I = current flowing through the metal

4.3 POTENTIODYNAMIC PLOT

A potentiodynamic plot (Figure A11, Page A.30) is obtained if the potential of the working electrode, starting from the corrosion potential, is slowly scanned in the anodic direction.

At a certain potential, the so called primary passivation potential (E_{pp}), the current potential curve changes direction and the dissolution current starts decreasing rapidly with increasing potential.

Once the metal is passivated the dissolution current (I_{pass}) is negligible, usually two to three orders of magnitude lower than the critical current density (the maximum in the region in which the corrosion current increases with increasing potential). The potential range over which the current remains at a low value is termed the passive potential range.

If the applied potential is further increased in the positive direction another potential will be reached at which the measured current will again begin to increase. This potential is strongly dependent on the corrosiveness of the medium.

4.4 PITTING SCAN

Pitting is a localised form of corrosion in which only small areas of the metal surface are attacked whilst the remainder is largely unaffected.

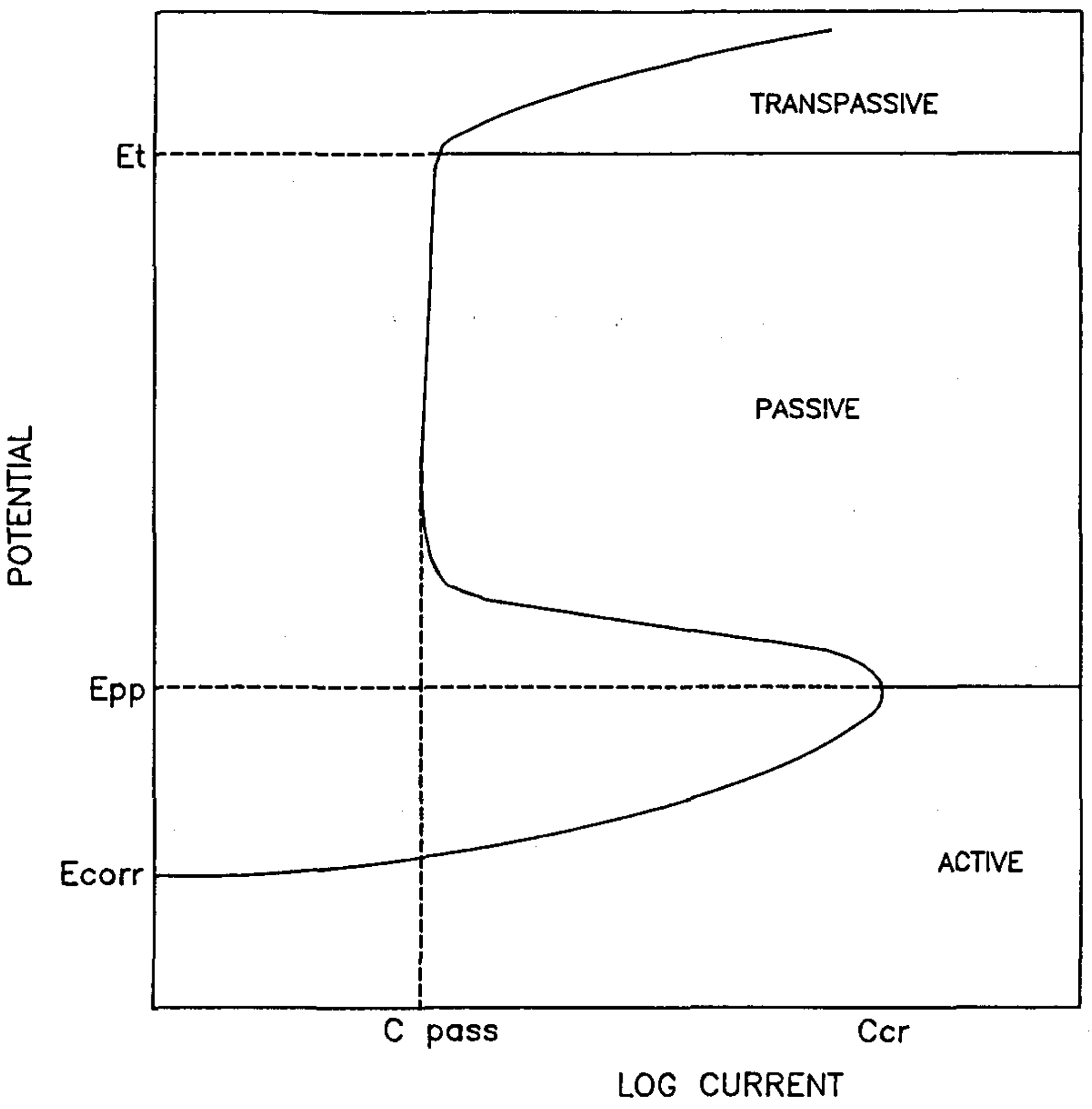

Figure A11 Potentiodynamic Plot

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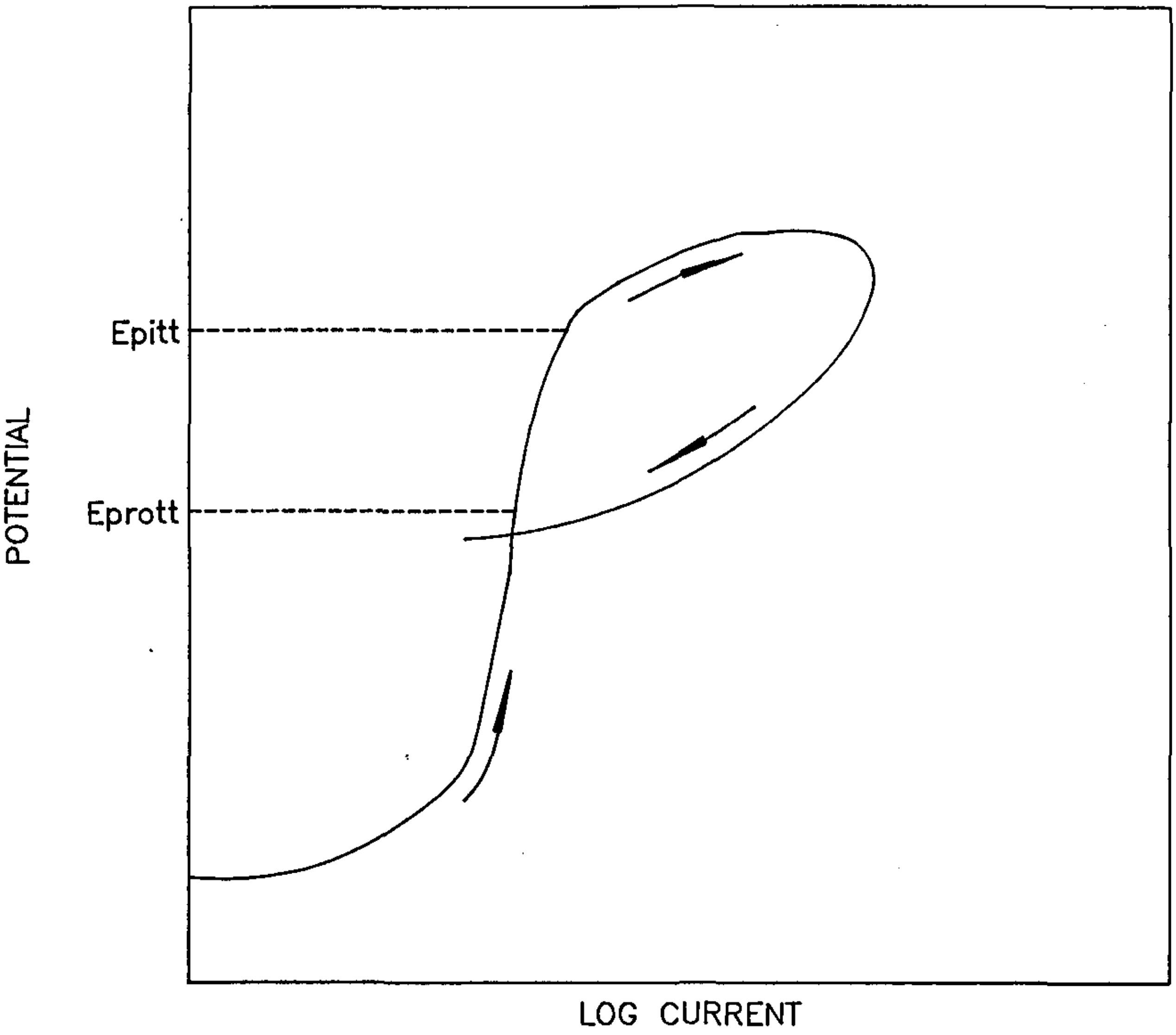

Figure A12 Typical Pitting Scan

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A pit is usually initiated by the adsorption of activating anions, particularly chloride ions, on defective sites in the surface oxide film, but for pitting attack to occur on a metal a certain corrosion potential, the pitting potential, E_{pitt}, must be obtained (Figure A12, Page A.31). This potential may be regarded as the most negative potential to cause the initiation and propagation of one or more pits.

In a pitting scan the potential, starting from E_{corr}, is slowly scanned in the positive direction to a predetermined current value above E_{pitt}, at which time the potential scan is reversed.

There are hysteresis on the reverse potential scan as pits continue to grow until the current is reduced to the original passive value. The potential at this intersection is called the protection potential against pitting, E_{prot}. Since below E_{prot} the metal will not pit and the whole surface will remain passive.

The difference between E_{pitt} and E_{prot} may be understood in this way: E_{prot} is always more negative than E_{pitt}, and whereas pitting will occur on a pit free surface above E_{pitt}, it will only occur in the range of potentials between E_{prot} and E_{pitt} if the surface is already pitted, i.e. between E_{prot} and E_{pitt} existing pits will continue to propagate, but initiation of new ones will not be possible.

5. CORROSION INDICES

In the discussions of corrosion indices to follow a short summary of the background of each index is given, as well as the formula, and interpretation of the calculated values where applicable. The indices that will be discussed are:

- Langelier Saturation Index (1936)
- Ryznar Stability Index (1944)
- Riddick Corrosion Index (1944)
- Casil Index (1948)
- Driving Force Index (1960)
- Larson Index (1975)
- Feigenbaum, Gal-or, Yahalom (1978)
- Aggressive Index (1980)
- Calcium Carbonate Precipitation Potential (1990)

5.1 LANGELIER SATURATION INDEX (LSI)

This index was developed by Prof W F Langelier of the University of California and presented at a convention of the A.W.W.A, held in Los Angeles in June 1936. (De Martini, 1937). The index provide a means of predicting if a water would deposit a thin film of calcium carbonate on pipe walls. If so, the pipe would be protected from corrosion. Its formula (Singley *et al.*, 1985) is;

$LSI = pHa - pHs$

were:

pHa = actual pH

pHs = $A^1 + B^1 - \log Ca^{2+} - \log Talk$

- A^1 = a function of water temperature
- B^1 = a function of ionic strength
- Both Ca^{2+} and total alkalinity (Talk) concentrations in mg/ℓ as $CaCO_3$.

A laboratory method to determine pHs is discussed in Addendum E.

The LSI is interpreted as follows:

LSI	>0:	Non-corrosive for hot water
	$>-0,5$:	Non-corrosive for cold water. In both the cases the water is super saturated with respect to $CaCO_3$.
LSI	$= 0$:	Water neutral. At equilibrium with respect to $CaCO_3$.
LSI	$= <0$:	Water corrosive. Under saturated with respect to $CaCO_3$.

The equation of pHs above is a simplified equation of Prof Langelier's original equation *viz.*

$$pHs = (pK_2^1 - pK_s^1) + pCa + p\left\{Alk + (H^+) - \frac{\underline{Kw}}{(H^+)}\right\} + \log\left\{1 + \frac{\underline{2K_2^1}}{(H_s^1)}\right\}$$

- pK_2^1 and pK_s^1 are the negative logarithms of the second dissociation constant for carbonic acid, and the activity product of $CaCO_3$, respectively.
- pCa is the negative logarithm of the molal concentration of calcium.
- pAlk is the negative logarithm of the equivalent concentration of titratable base.
- H^+ = molal concentration of H^+ in the water when at actual pH.
- H_s^+ = molal concentration of H^+ in the water when it is at pHs.

Between pH 6,5 and 9,5 the correction to Alk for H^+ is small and all terms containing (H^+) can thus be omitted (De Martini, 1937). It is also important to note that the LSI is not suitable for use in soft, saline waters where a low buffer capacity, and ionic species such as chlorides, may disrupt the $CaCO_3$ equilibrium conditions (Singley, 1989).

5.2 RYZNAR STABILITY INDEX (RSI)

John W Ryznar, Research Chemist of the National Aluminate Corporation, Chicago developed his index in 1944. Ryznar (1944) based the index on scale formation in distribution mains, domestic hot water heaters, boiler feed water heaters, locomotive injectors and boiler feed water lines. Most of his laboratory investigations were based on scale information in glass coils on water with temperatures ranging from ± 50°C to ± 90°C. One reason for Ryznar's attempt to developed a new index was that the LSI is not always reliable in predicting scale formation, because in some cases where the LSI indicated positive values or scale formation, no scale formation occurred and corrosion were experienced. This can be seen more clearly by assuming two waters with the following characteristics.

(a) Water at 75°C, pHs = 6,0 and actual pH = 6,5
LSI = +0,5.

(b) Water at 75°C, pHs = 10,0 and actual pH = 10,5
LSI = +0,5

From the saturation index it might be predicted that both waters would be equally prone to scale formation. In reality (a) would be scale forming, while (b) would be quite corrosive. (See equation for pHs in 5.1). At pHs of 6,0 the calcium and total alkalinity of the water aught be high, while at pHs of 10,0 the calcium and total alkalinity should be low.

In order to eliminate the possibility of misinterpreting a positive LSI as being non-corrosive or scale forming, a new empirical expression 2pHs - pH, was proposed by Ryznar. The value obtained by the expression 2pHs - pH was called the Stability Index for convenience. Using the example (a) and (b) above the following values would be obtained for the Stability Index.

	Saturation Index	Stability Index
Water (a)	+0,5	+5,5
Water (b)	+0,5	+9,5

The Stability Index will be positive for examples (a) and (b). Experimental results indicated that different types of water with a Stability Index value of 5,5 will give an appreciable amount of calcium carbonate scale. Water having a Stability Index value of 9,5 on the other hand, will form only a limited amount of calcium carbonate scale and may be severely corrosive.

The calculated RSI values are interpreted as follows:
RSI >8 : increasingly severe corrosion
RSI = 7 : no corrosion or scaling
RSI <6 : scaling

5.3 RIDDICK CORROSION INDEX (RCI)

The Riddick Corrosion Index (Riddick, 1944) is an empirically based formula that weights several factors that influence, including dissolved oxygen, chloride ion concentration, non-carbonate hardness and silica. It is defined as follows:

$$\mathrm{RCI} = \frac{75}{\mathrm{Alk}}\,[\mathrm{CO_2} + 0{,}5\,(\mathrm{hardness} - \mathrm{Alk}) + \mathrm{Cl^-} + \mathrm{NO_3^-}]\;\{10/\mathrm{SiO_2}\}\;\{(\mathrm{DO} + 2)/\mathrm{DOsat}\}$$

where:
Hardness, Alk and CO_2 are expressed as mg/ℓ $CaCO_3$;
N as mg/ℓ NO_3^-; All other parameters are in mg/ℓ

The proposed interpretation of measured RCI values are as follows:

RCI less or equal to 5, - extremely non corrosive
RCI between 6 and 25 - non-corrosive
RCI between 26 and 50 - moderately corrosive
RCI between 51 and 75 - corrosive
RCI between 76 and 100 - very corrosive
RCI greater than 100 - extremely corrosive

The Riddick Corrosion Index attempts to relate water solubility parameters to the corrosiveness of the solution. Results obtained with this index correlate well with the corrosivity of soft water, but less so with that of hard waters.

5.4 CASIL INDEX (CI)

The Casil Index was proposed by Loschiavo in 1948 and is a modification of the calcium carbonate solubility equation to account for the effect of other parameters in soft water (Singley, 1985). It predicts the corrosiveness by using a cation/anion balance. As cations decrease, the index values decrease, indicating more corrosive conditions. As anions increase in concentration the index values decrease indicating more corrosive conditions. The Casil index is defined as:

$$CI = Ca^{2+} + Mg^{2+} + HSiO_3^- - \text{Anions}/2$$

Concentration are expressed in milli equivalents per litre.

The calculated CI values are interpreted as follows:

CI <0 very corrosive water
CI >0 $<0,1$ indicate slightly corrosive waters.
CI $>0,1$ indicate non-corrosive water

A reduction in pH through acid addition adds corrosive anions (i.e. Cl^- or SO_4^{2-}), which lowers the CI and thus indicates increasing corrosiveness.

5.5 DRIVING FORCE INDEX (DFI)

This index was developed by McCauley in 1960 and is another of the calcium carbonate saturation indices. It is based on the ratio of $CaCO_3$ ion product in solution and that which would exist in equilibrium (Singley, 1985). The formula is:

$$\text{DFI} = [Ca^{2+}]\,[CO_3^{2-}]/K_{sol} \times 10^{10}$$

where:
Ca^{2+} and CO_3^{2-} are expressed in mg/ℓ as $CaCO_3$. K_{sol} is the solubility product of $CaCO_3$.

The DFI is interpreted as follows.

DFI values between 0 and 0,1 indicate slightly corrosive water
DFI values >0,1 indicate non-corrosive water

5.6 LARSON INDEX (LI)

This index was developed by Dr T E Larson of the Illinois State Water Survey, Urbana in 1975. It is an attempt to measure the aggressive nature of specific ions such as chloride and sulphate that forms strong acids in anodic pits where the exposed metal is corroded. Bicarbonates form weak acids and precipitate a protective scale. The Larson Index is defined as:

$$LI = (C\ell^{-} + SO_4^{2-})/\text{Talk}$$

were $C\ell^{-}$ and SO_4^{2-} are the chloride and sulphate concentrations, respectively, and Talk represents total alkalinity. All concentrations are expressed in terms of mg/ℓ of equivalent $CaCO_3$. When the ratio of reactive anions to alkalinity is greater than 0,5 the possibility of corrosive action exists. Unlike the LSI, this index does not refer to the solubility of $CaCO_3$, but rather to the faster rates of corrosion of metals because of the effects of conductivity. It is not applicable in soft waters (Singley, 1985).

5.7 FEIGENBAUM, GAL-OR, YAHALOM INDEX (Y)

This index is most relevant to hard saline waters and was developed in Israel by Feigenbaum and co-workers using waters of the Negev Desert region (Feigenbaum, 1978). Correlation of scale impedance and water quality factors were investigated. It stresses the important role structure and porosity of natural calcium-iron scales play in the corrosion process. It also indicates that high chloride and sulphate concentrations (500 - 800 mg/ℓ), while conventionally regarded as corrosion enhancing factors, may assist in more dense crystal growth of calcium carbonate in pipe systems, thus leading to better corrosion protection. With low chloride and sulphate concentrations (<200 mg/ℓ) the crystal growth is more porous of nature and will render less corrosion protection.

The index is a combination of the ratio:

$$\frac{(Ca^{2+})\,(HCO_3^{-})^2}{(CO_2)}$$

which represents the $CaCO_3$ precipitation equilibrium in the reaction:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3\ (s) + CO_2\ (g) + H_2O$$

and the Larson Index. When corrected for low hardness the result is:

$$Y = A_2H + B\ [C\ell^- + SO_4^{2-}]\ \exp\ (-1/A_2H) + C_1$$

where:
A_2 = 0,00035
B = 0,34
C_l = 19,0
H = $(Ca^{2+})\ (HCO_3^-)^2 /\ (CO_2)$

$C\ell^-$, SO_4^{2-}, Ca^{2+} and CO_2 expressed in mg/ℓ and HCO_3^- as mg/ℓ $CaCO_3$.

Field tests indicate less corrosion with higher calculated values, that may be generalised as follows:

$Y > 500$ - mild corrosion
$Y = 200$ to 500 - moderate corrosion
$Y < 200$ - high corrosion

This method has not been tested widely.

5.8 AGGRESSIVE INDEX (AI)

The Aggressive Index is a simplification of the Langelier Index and was developed by the AWWA Standards Committee for asbestos - cement pipes in contact with water and other liquids (1980). The formula is as follows:

$$AI = pH + \log AH$$

Where:
A = Total alkalinity as mg/ℓ $CaCO_3$
H = Calcium hardness as mg/ℓ $CaCO_3$

The interpretation of the values obtained are as follows:

$AI > 12,0$ - water is non aggressive
$AI = 10,0$ to 11,9 - water is considered moderately aggressive.
$AI < 10,0$ - water is highly aggressive.

The requirement for the use of alkalinity, hardness and pH terms in the equation can be explained as follows. If a large disparity in concentrations is present between two phases, concrete and water, the reaction will proceed rapidly in the direction required to establish equilibrium. For soft water the concentration gradient becomes very high and calcium present in concrete as $Ca(OH)_2$ will dissolve rapidly. On the other hand, where water already contains high concentrations of calcium, the concentration gradients are lower or can disappear when saturation of the water phase is achieved. This explains why for high values of hardness the AI values becomes higher and the water therefore less aggressive. Relatively insoluble carbonates originally present on concrete surfaces will not dissolve so easily if the alkalinity and pH of the water is high, because this will ensure high carbonate (CO_3^{2-}) concentrations in the water. High pH values will also ensure high hydroxide concentrations in the water preventing $Ca(OH)_2$ in the concrete from dissolving (Basson, 1989).

5.9 CALCIUM CARBONATE PRECIPITATION POTENTIAL (CCPP)

This index is a theoretical prediction of the amount of $CaCO_3$ in mg/ℓ, that can precipitate, or dissolve, in a given water. The calculation of this index is complex (Merril, 1990) and can only be applied with the aid of a computer program (Appendix D: 2.2.1). Determinations required for calculating CCPP are calcium as Ca^{2+}, alkalinity as mg/ℓ $CaCO_3$, pH, temperature in °C and total dissolved solids (TDS). This index is valid over the entire range of pH values. The CCPP of a water can, however, also be determined by a laboratory method as described in Appendix H.

5.10 RELATIONSHIP BETWEEN INDICES

The relationship between the LSI, AI, RI, DFI and CCPP indices are shown in Figure A13, after Rossum (1983). While the CCPP index predicts fairly accurately the amount of $CaCO_3$ that will precipitate or dissolve, the LSI, AI and RI predictions are totally erroneous and can only be applied to indicate if a water is over or under saturated with respect to calcium carbonate. The DFI, however, conforms more to the CCPP index for $pH > 8{,}45$.

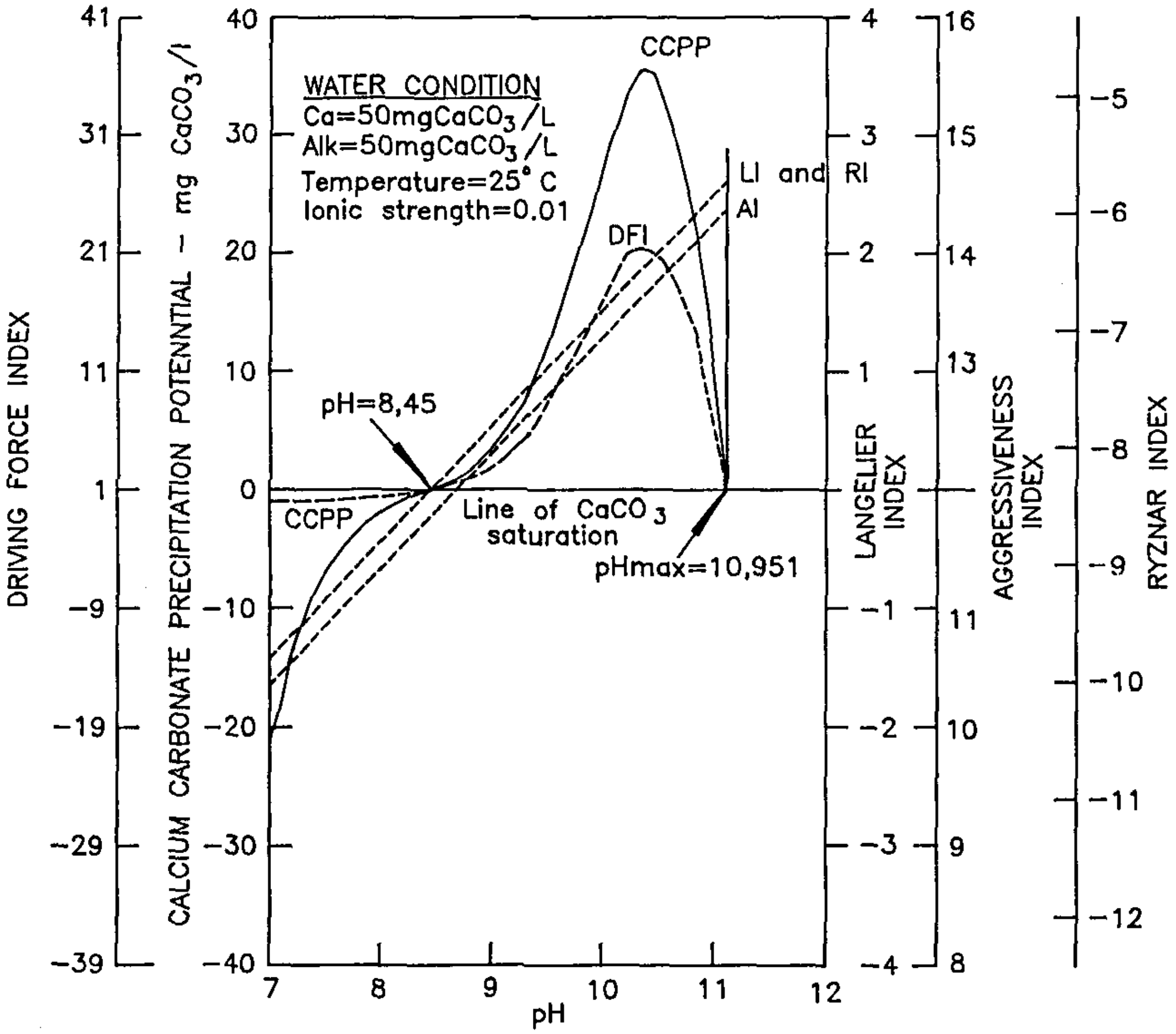

Figure A13 Indices values versus pH

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APPENDIX B

THEORETICAL DETERMINATION OF A VARIETY OF CARBONIC SPECIES

APPENDIX B

THEORETICAL DETERMINATION OF A VARIETY OF CARBONIC SPECIES

As the concentrations of the different carbonic species are used in the equations for the indices, formulae had to be developed to calculate the required concentrations of various species from the results of the available determinants, e.g. alkalinity, pH, temperature and total dissolved solids (TDS). Symbols used below are defined in Table of contents of main document page v.

1. DETERMINATION OF $[H_2CO_3]$ $[HCO_3^-]$ AND (H^+)

(If the total carbonic content of the water is known)

From the equilibria of carbonic acid:

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

and

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

it follows that

$$K_1 = \frac{(HCO_3^-)(H^+)}{(H_2CO_3)} \quad \text{(B1)}$$

$$K_2 = \frac{(CO_3^{2-})(H^+)}{(HCO_3^-)} \quad \text{(B2)}$$

K_1 and K_2 are thermodynamic equilibrium constants and (HCO_3^-), etc are active molar concentrations. To rewrite these concentrations in terms of stoichiometric molar concentrations, fi, a factor called the activity coefficient is provided, so that (B1) and (B2) become

$$K_1 = \frac{fm[HCO_3^-](H^+)}{(H_2CO_3)} \quad \text{(B3)}$$

$$K_2 = \frac{fd[CO_3^{2-}](H^+)}{fm[HCO_3^-]} \quad \text{(B4)}$$

fi for monovalent ions becomes fm, and fi for divalent ions becomes fd.

(H^+) is not rewritten in mol/ℓ because it is measured directly with a pH meter. Factors K_1 and K_2 are temperature dependent and fd and fm are temperature and ionic strength dependent. The ionic strength (μ) can be determined from equations;

$$\mu = 2{,}5 \times 10^{-5}\ Sd$$

where Sd is the TDS of the sample (Lowewenthal, 1983).

The total carbonic concentration, Ct, is

$$Ct = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \tag{B5}$$

By substituting equations (B3) and (B4) into equation (B5) the different carbonic concentrations are obtained as follows:

$$[H_2CO_3] = Ct/[1 + K_1/fm\ (10^{-pH}) + K_1K_2/fd\ (10^{-pH})^2]$$

$$[HCO_3^-] = Ct/[1 + 10^{-pH}.fm/\{K_1 + K_2.fm(10^{-pH}).fd\}]$$

$$[CO_3^{2-}] = Ct/[1 + (10^{-pH})^2.fd/K_1 - K_2 + (10^{-pH}).fd/K_2.fm]$$

where $10^{-pH} = (H^+)$

2 DETERMINATION OF $[HCO_3^-]$ AND $[CO_3^{2-}]$

(If the total alkalinity of the water is known)

The total alkalinity (Talk) is the sum of the bicarbonate, carbonate and hydroxide concentrations expressed in mg/ℓ $CaCO_3$.

$$Talk = ([HCO_3^-]/2 + [CO_3^{2-}] + [OH^-]/2 - (H^+)/2) \times 10^5 \tag{B6}$$

The denominators, 2, in equation (B6) serve to convert the concentrations of OH^- and H^+ into equations of $[CaCO_3]$, and factor 10^5 serves to convert the $[CaCO_3]$ into mg/ℓ$CaCO_3$. From equation (B6), $[HCO_3^-]$ and $[CO_3^{2-}]$ can be calculated as follows:

$$Talk - ([OH^-]/2 - (H^+)/2) \times 10^5 = [HCO_3^-] \times 10^5/2 + [CO_3^{2-}] \times 10^5 \tag{B7}$$

Thus

$$Talk \times 10^{-5} - ([OH^-]/2 - (H^+)/2) = [HCO_3^-]/2 + [CO_3^{2-}] \tag{B8}$$

2.1 DETERMINATION OF $[HCO_3^-]$

Substitute (B4) into (B8):

$$Talk \times 10^5 - ([OH^-]/2 + (H^+)/2) = [HCO_3^-]/2 + K_2\ fm\ [HCO_3^-]/fd\ (H^+)$$

Therefore

$$[HCO_3^-] = \{Talk \times 10^5 - [OH^-]/2 - (H^+)/2)\}/\{0{,}5 + K_2 fm/fd(H^+)\} \tag{B9}$$

2.2 DETERMINATION OF $[CO_3^{2-}]$

Substitute (B4) into (B8)

$$Talk \times 10^5 - ([OH^-]/2 - (H^+)/2) = [CO_3^{2-}]\,(H^+)fd/2K_2.fm + [CO_3^{2-}]$$

Therefore

$[CO_3^{2-}] = \{Talk \times 10^{-5} - [OH^-]/2 - (H^+)/2\}/\{fd(H^+)/2K_2.fm + 1\}$ . . . . (B10)

Let

$X_1 = Talk \times 10^{-5} - ([0H^-]/2 - (H^+)/2)$
$Y_1 = 0{,}5 + K_2fm/fd(H^+)$
$Z_1 = fd(H^+)/2\,K_2.fm + 1$
$(H^+) = 10^{-pH}$
$[OH^-] = 10^{pH-pKw}/fm$

2.3 DETERMINATION OF $[H_2CO_3]$

From equation (B3) follows

$[H_2CO_3] = fm\,[HCO_3^-]\,(H^+)/K_1$ . . . . (B11)

Substitute equation (B9) into equation (B11)

$[H_2CO_3] = fm\,(10^{-pH})X_1/K_1\,Y_1$ . . . . (B12)

3. DETERMINATION OF OTHER RELATED ENTITIES

3.1 DETERMINATION OF TOTAL CARBONIC CONCENTRATION, Ct

$$Ct = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

Thus

$$Ct = fm(10^{-pH})X_1/Y_1K_1 + X_1/Y_1 + X_1/Z_1$$

Therefore

$Ct = X_1\{fm(10^{-pH})/Y_1K_1 + 1/Y_1 + 1/Z_1\}$ . . . . (B13)

The total carbonic concentration can also be determined from Loewenthal (1982)

$Ct = (Talk + Tacid)/2$ . . . . (B14)

3.2 DETERMINATION OF TOTAL ACIDITY

The total acidity can be determined from

$Tacid = 2[H_2CO_3] + [HCO_3^-] + [H^+] - [OH^-]$

As mol/ℓ (Loewenthal, 1982) and

$Tacid = ([H_2CO_3] + [HCO_3^-]/2 + (H^+)/2 - [OH^-]/2)x10^5$

as mg/ℓ $CaCO_3$

Thus

$Tacid = (fm(10^{-pH})X_1/Y_1K_1 + X_1/2Y_1 + 10^{-pH}/2 - 10^{pH-pKw}/2fm)X10^5$ . . . . (B15)

3.3 DETERMINATION OF TOTAL ALKALINITY

The total alkalinity can be determined by

$Talk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$ . . . . (B16)

as mol/ℓ(Loewenthal, 1982) and

$Talk = ([HCO_3^-]/2 + [CO_3^{2-}] + [OH^-]/2 - (H^+)/2) x10^5$

as mg/ℓ $CaCO_3$

3.4 DETERMINATION OF FREE CO_2

The free CO_2 concentration (Loewenthal, 1982) is directly related to the $[H_2CO_3]$.

Thus

$[H_2CO_3] = fm (10^{-pH}) X_1/Y_1K_1 \approx [C0_2]$ . . . . (B17)

Free CO_2 as mg/ℓ CO_2

From equation (B17) it follows that if $[H_2CO_3]$ can be determined the result will be about equal to $[CO_2]$

Thus

$[CO_2] X 44 x 1000 = 4{,}4 x 10^4 [CO_2] =$ mg/ℓ as CO_2 . . . . (B17a)

Free CO_2 as mg $CaCO_3$/ℓ

From equation (B17) it follows that if $[H_2CO_3]$ can be determined the result will be about equal to $[CO_2]$.

Thus

$[CO_2] x 100 x 1000 = [CO_2]X10^5 =$ mg/ℓ as $CaCO_3$ . . . . (B17b)

3.5 DETERMINATION OF THE CALCIUM CARBONATE SATURATION STATE - SS

From the solubility equilibrium of calcium carbonate (Loewenthal, 1982)

$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$

with Ksol the activity constant, it follows that

$Ksol = (Ca^{2+})(CO_3^{2+})/(CaCO_3)$ . . . . (B18)

Equation (B18) can be rewritten in terms of mol/ℓ thus:

$Ksol = fd\ [Ca^{2+}]fd[CO_3^{2-}]/[CaCO^3]$

Therefore

$[Ca^{2+}][CO_3^{2-}] = Ksol\ /fd^2 = K^1sol$ . . . . (B19)

With K^1sol the solubility equilibrium constant.

Because the valence for $CaCO_3$ is zero, fi for $[CaCO_3] = 1$ or $[CaCO_3]$ can also be taken as unity because it does not dissolve.

If the $[CO_3^{2-}]$ in the water is known, the $[Ca^{2+}]$ can be determined from equation (B19). If the difference between the true calcium content and the calculated calcium, both as mg/ℓ as $CaCO_3$, is positive, the water is over saturated, and if the difference is negative the water is under saturated with respect to calcium carbonate.

Thus

$CaCO_3^-$ SS in mg/ℓ $CaCO_3 = Ca^{2+} \times 2{,}5 - \dfrac{K^1sol \times 10^5}{X_1/Z_1}$ . . . . (B20)

with $[CO_3^{2-}] = X_1/Z_1$, and Ca^{2+} as obtained from chemical analysis.

4. REMARKS

To evaluate the equations developed by Rand Water as described in the paragraphs above, results obtained were compared with those obtained with the Caldwell-Lawrence diagrams (figure B1), the alkalinity-acidity-pH equilibrium diagrams (figure B2), Loewenthal (1982) and the CO_2-nomograph (figure B3), Standard Methods (1975) for the same water samples. In all cases the results obtained with the equations were the same as those obtained with the diagrams and nomograph.

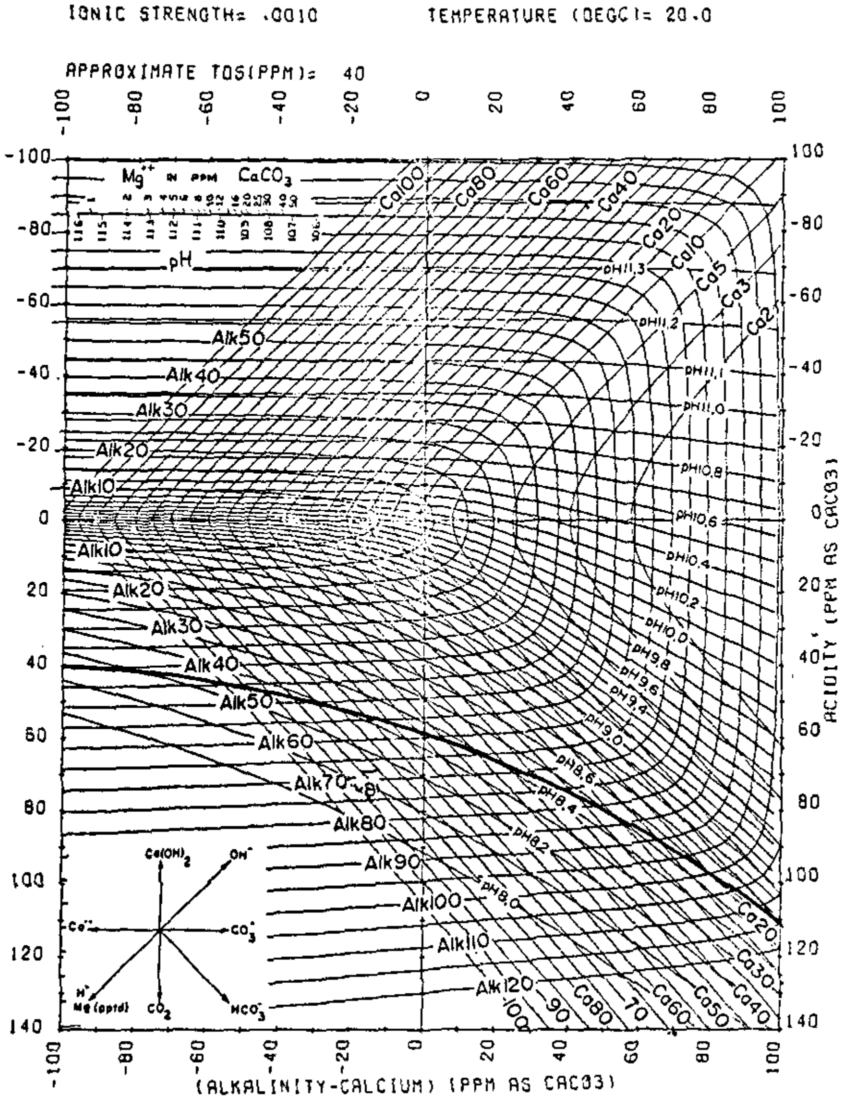


FIGURE B1 CALDWELL-LAURENCE DIAGRAM

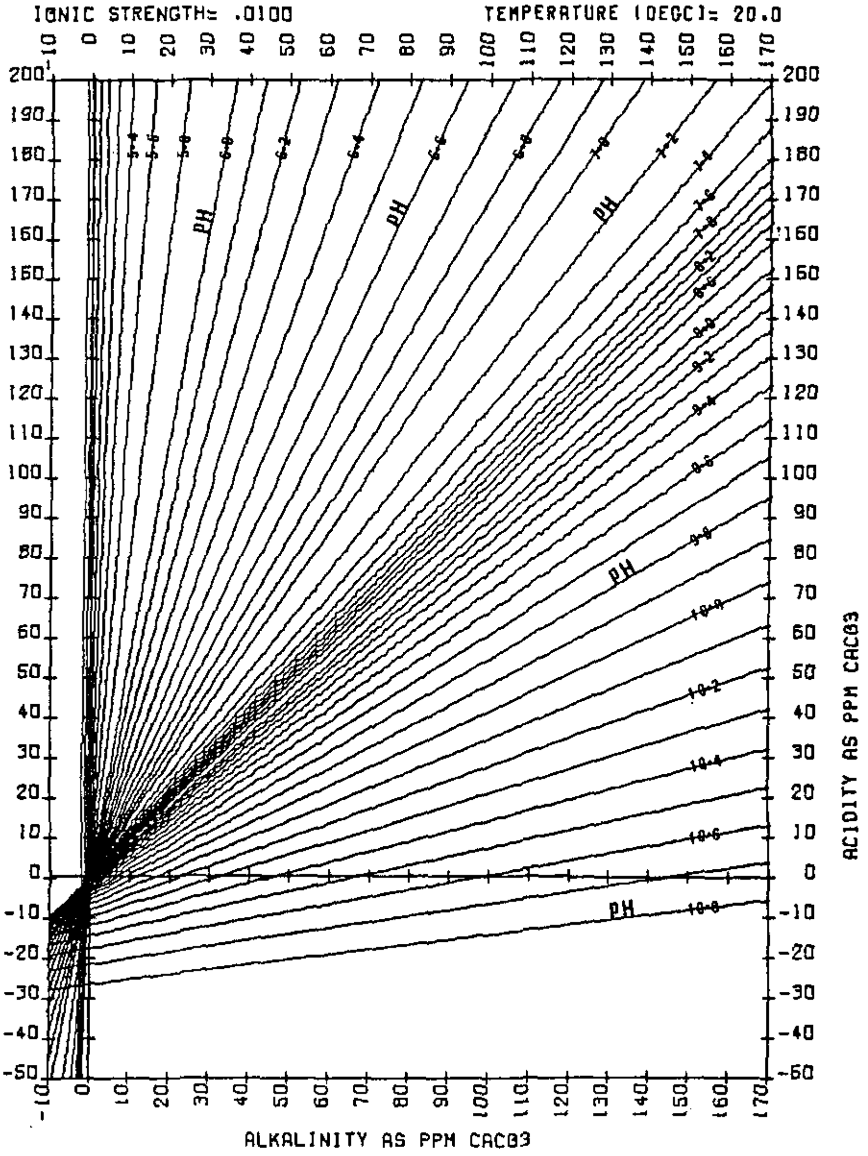
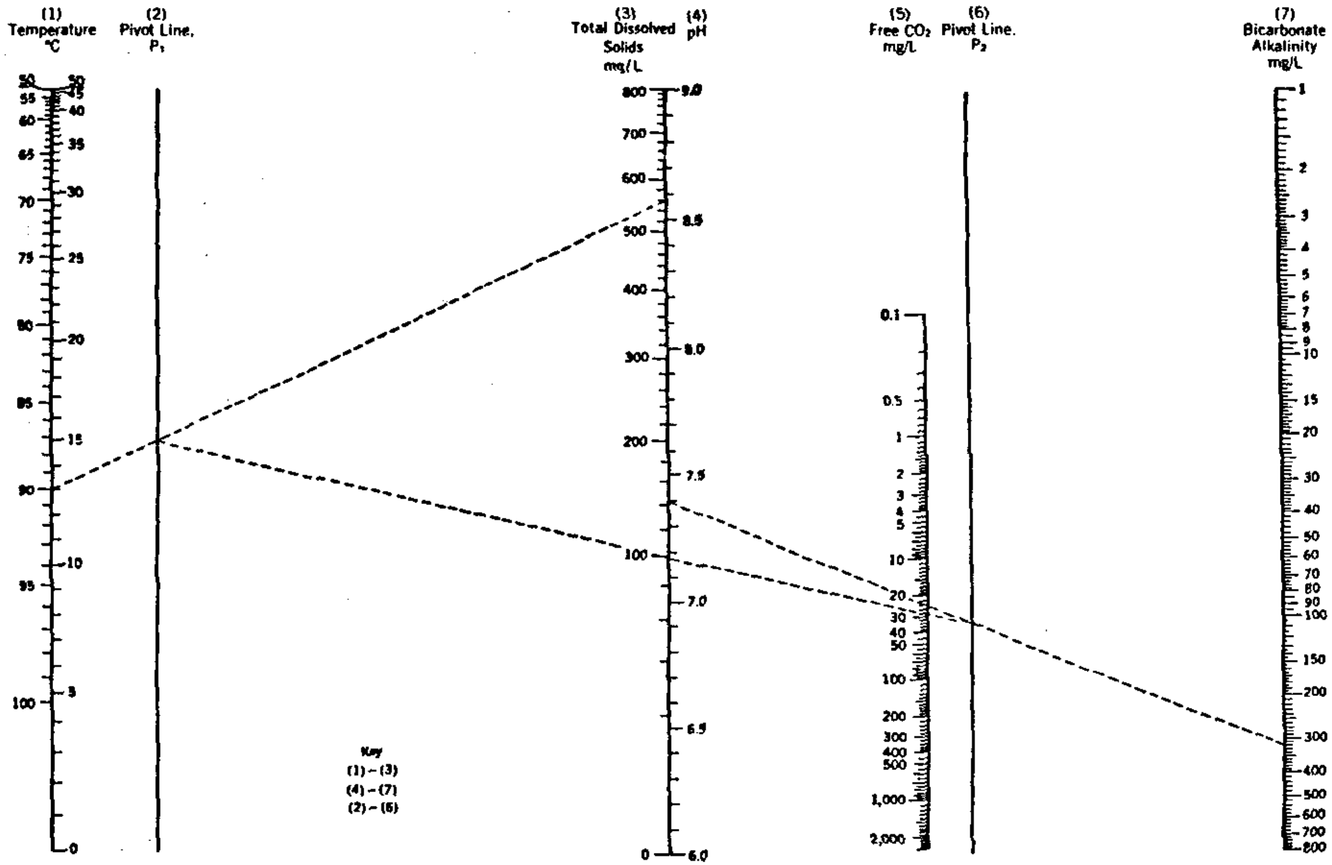


FIGURE B2 ALKALINITY - ACIDITY - pH EQUILIBRIUM



Nomograph for evaluation of free carbon dioxide content. To use: Align temperature (Scale 1) and total dissolved solids (Scale 3), which determines Point P_1 on Line 2; align pH (Scale 4) and bicarbonate alkalinity (Scale 7), which determines Point P_2 on Line 6; align P_1 and P_2 and read free carbon dioxide on Scale 5. (Example: For 13°C temperature, 560 mg total dissolved solids/L, pH 7.4, and 320 mg alkalinity/L, the free carbon dioxide content is found to be 28 mg/L.)

FIGURE B3: NOMOGRAPH FOR EVALUATION OF CARBONATE ALKALINITY

APPENDIX C

DETAILED DISCUSSION OF THE RELATIONSHIP BETWEEN CALCULATED INDICES VALUES AND INITIAL MEASURED CORROSION RATES

APPENDIX C

DETAILED DISCUSSION OF THE RELATIONSHIP BETWEEN CALCULATED INDICES VALUES AND INITIAL MEASURED CORROSION RATES

1. PRELIMINARY INVESTIGATION WITH CORRATER MODEL 1120

The discussion of the relationship between calculated indices values and initial measured corrosion rates are based on the results obtained in the preliminary investigation with the Corrater model 1120 (par 3.1 of main document). The equations of the indices will be shown and a relationship between the obtained corrosion rate measurements and increasing concentrations of different chemical components will be drawn. An explanation for the tendencies, related to the equations will be given, where possible.

1.1 Ryznar Stability Index (RSI)

Equation: $RSI = 2pHs - pH$
with $pHs = A + B - \log(Ca^{2+}) - \log(Talk)$

a) For increasing concentration of chloride and sulphate the:

i) Corrosion rate increases logarithmical
ii) Calculated index values increases logarithmical (possible indication of increasing corrosiveness).

The term B in the equation above will increase logarithmically because the ionic strength increases logarithmically with the increase of Cl^- and SO_4^{2-} concentrations, thus RSI will also increase logarithmically.

b) For increasing calcium and alkalinity (HCO_3^-) concentrations the:

i) Corrosion rate increases logarithmically
ii) Calculated index values decreases logarithmically (decreasing corrosiveness)

The combination of the term B and $-\log(Ca^{2+})$ or $-\log(Talk)$ will result in RSI values decreasing logarithmically.

c) Comment

The measured corrosion rates follow the same pattern as the calculated RSI values for increasing Cl^- and SO_4^{2-} concentrations for which only the ionic strength term in the RSI equation are affected. For Ca^{2+} and HCO_3^- the negative terms, $-\log(Ca^{2+})$ and $-\log(Talk)$, are affected and for this reason the tendency for the calculated RSI values are opposite to those obtained for Cl^- and SO_4^{2-}.

1.2 Langelier Saturation Index (LSI)

Equation: LSI = pH - pHs

a) For increasing concentrations of <u>chloride</u> and <u>sulphate</u> the:

   i) Corrosion rate increases logarithmically
   ii) Calculated index values increase logarithmically (increasing corrosiveness)

   The term B in the equation will increase logarithmically; thus LSI will decrease indicating higher corrosivity.

b) For increasing <u>calcium</u> and <u>alkalinity</u> (HCO_3^-) concentrations the:

   i) Corrosion rate increases logarithmically
   ii) Calculated index values decreased logarithmically (decreasing corrosiveness)

   The combination of the term B and -log (Ca^{2+}) or -log (Talk) will result in increasing LSI values indicating lower corrosiveness.

c) <u>Comment</u>
   The comments are the same as for the RSI.

1.3 <u>Aggressive Index (AI)</u>
Equation: AI = log AH

a) For increasing concentrations of <u>chloride</u> and <u>sulphate</u> the:

   i) Corrosion rate increases logarithmically
   ii) Calculated index values show no tendency or effect

   Chloride and sulphate do not feature in the above equation and thus will have no effect on the calculated AI values.

b) For increasing <u>calcium</u> and <u>alkalinity</u> (HCO_3^-) concentrations the:

   i) Corrosion rate increases logarithmically
   ii) Calculated index values increases logarithmically (decreasing tendency to dissolve carbonate)

c) <u>Comment</u>
   Calcium and alkalinity are represented in the equation of AI but shows the opposite tendency than the measured corrosion rates.

1.4 <u>Driving Force Index (DFI)</u>
Equation: DFI = $(Ca^{2+})(CO_3^{2-})/K_{sol}\ 10^{10}$

a) For increasing concentrations of chloride and sulphate the:

  i) Corrosion rate increases logarithmically
  ii) Calculated index values decrease logarithmically (increasing corrosiveness)

Chloride and sulphate are not represented in the DFI equation but effects the ionic strength of the solution. If the ionic strength increases (chloride and sulphate increases) the activity coefficient (fi) decreases. If fi decreases then ks increases; therefore DFI will decrease.

b) For increasing concentrations of calcium and alkalinity (HCO_3^-) the:

  i) Corrosion rate increases logarithmically
  ii) The calculated index values increase logarithmically (decreasing corrosiveness)

Calcium and alkalinity are incorporated in the DFI equation, and the DFI values calculated will therefore increase linearly with increase in concentrations, but Ksol increases logarithmically because of the logarithmical relationship between activity coefficient and ionic strength. Therefore the total effect is a logarithmic increase in DFI calculated values.

1.5 Larson Index (LI)

Equation $LI = (Cl^- \times SO_4^{2-})/Talk$

a) For increasing concentration of chloride and sulphate the:

  i) Corrosion rate increases logarithmically
  i)) Calculated index values increase linearly (increasing corrosiveness)

The calculated index values increase linearly because of a direct proportional relationship between the calculated values with both chloride and sulphate, as no term effected by ionic strength is present.

b) For increasing concentrations of calcium the:

  i) Corrosion rate increases logarithmically
  ii) The calculated index values are not affected

The calculated index values show no effect because calcium is not represented in the LI equation.

c) For increasing concentrations of alkalinity (HCO_3^-) the:

  i) Corrosion rate increases logarithmically

ii) Calculated index values decrease gradually (decreasing corrosiveness) and trends towards a constant value

The calculated index values trends towards a constant value because the alkalinity concentration approaches the sum of the chloride and sulphate concentrations.

1.6 Riddick's Corrosion Index (RCI)

Equation: $RCI = [75/Alk] \{CO_2 + 0{,}5\ (hardness - Alk) + C\ell^- + 2\ N\}\ (10/SiO_2)\ (DO + 2)\ /\ (DOsat)$

a) For increasing concentrations of chloride the:

i) Corrosion rate increases logarithmically
ii) Calculated index values increase linearly (increasing corrosiveness)

The relationship between the calculated index values and chloride is directly proportional and for this reason the relationship is linear.

b) For increasing concentrations of sulphate the:

i) Corrosion rate increases logarithmically
ii) Calculated index values decrease logarithmically (decreasing corrosion rate)

Sulphate does not appear in the equation. It is postulated that an increase in it's concentration will cause a decrease in the activity coefficient that will cause a decrease in the carbon dioxide or alkalinity concentration. This decrease is logarithmical.

c) For increasing concentrations of calcium the:

i) Corrosion rate increases logarithmically
ii) Calculated index values increase linearly (increasing corrosiveness)

The RCI values are directly proportional to the calcium (total hardness) concentration and for this reason the relationship is linear. The effect of carbon dioxide [CO_2] on the calculated index values is so small that it can be ignored.

d) For increasing concentrations of alkalinity (HCO_3^-) the:

i) Corrosion rate increases logarithmically
ii) Calculated index values decrease gradually (decreasing corrosiveness) with a trend towards constant values

The tendency of a gradual decrease with a trend toward constant values is caused by the combination of terms and factors,

75/Alk x 0,5 (Thard - Talk)

1.7 Feigenbaum/Gal-or/Yahalom (Y)

Equation: $Y = A_2H + B\ (Cl^- + SO_4^{2-})\ \exp(-1/A_2H) + C_1$
and $H = (Ca^{2+})(HCO_3^-)^2/(CO_2)$

a) For increasing concentrations of chloride and sulphate the:

i) Corrosion rates increases logarithmically
ii) Calculated index values increase linearly (decreasing corrosiveness)

Calculated index values increase linearly because of the direct proportional relationship between Y and Cl^- as well as SO_4^{2-} concentrations in the equation.

b) For increasing concentrations of calcium and alkalinity (HCO_3^-) the:

i) Corrosion rate increase logarithmically
ii) The calculated index values increase linearly (decreasing corrosion rate)

With the chloride and sulphate concentrations at zero, the equation simplifies to

$$Y = A_2\ (Ca^{2+})(HCO_3^-)^2/(CO_2) + C_1$$

In this format Y is directly proportional to the Ca^{2+} concentration. The CO_2 and HCO_3^- concentrations are assumed to be constant for all the samples at a constant temperature. The molar concentrations for CO_2 is about equal to the carbonic acid and bicarbonate ions for a constant pH, thus the factor $(HCO_3^-)^2/(CO_2)$ simplifies to HCO_3^-. If it is assumed that a small constant amount of Ca^{2+} is present the simplified equation indicates a linear relationship for Y values with increasing bicarbonate concentration.

1.8 Casil Index (CI)
Equation: $CI = Ca + Mg + HSiO_3^-$ Anions/2

a) For increasing concentrations of chloride and sulphate the:

i) Corrosion rate increases logarithmically
ii) Calculated index values decrease linearly (increasing corrosiveness)

The calculated CI values, are directly proportional to the chloride or sulphate concentrations.

b) For increasing concentrations of calcium the:

  - i) Corrosion rates increases logarithmically
  - ii) Calculated index values increase linearly (decreasing corrosion)

c) For increasing concentrations of alkalinity (HCO_3^-) the:

  - i) Corrosion rates increase logarithmically
  - ii) Calculated index values decrease linearly (increasing corrosiveness)

d) Comment

The reason for the opposite tendencies, as calculated for calcium and alkalinity, is because calcium is part of the positive, and alkalinity, part of the negative terms in the equation.

2. OBSERVATIONS

A very important observation that follows from the above discussion is the logarithmic tendency with changing salt concentrations for the calculated Ryznar, Langelier, Driving Force, and Riddick corrosion indices, all containing factors or terms dependent on the ionic strength of the samples. These logarithmic tendencies also correlate with the logarithmic tendencies for the corrosion rates.

A second observation is that for participating determinant concentrations up to a 100 mg/ℓ, the increase in corrosion rate is directly proportional to the increase in concentration.

A third observation, which is true for all the different determinants, is that the initial corrosion rates increase with increasing salt concentration, while the calculated indices values only increase for chloride and sulphate, and decrease for calcium and alkalinity. A summation of the similarities between the initial measured corrosion rates and calculated indices values are depicted in table 3.1.1 paragraph 3.1 in main document. From these similarities it is clear that no single index accounts for the effects of all the determinants on corrosion rates.

In samples containing chloride and sulphate in different ratios, paragraph 3.1.2 in main document, the corrosion rates follow the same tendency as the calculated values for the Larson and Casil Indices.

APPENDIX D

DETAILED DISCUSSION OF THE EFFECT OF VARIOUS DETERMINANTS AND CONCENTRATIONS THEREOF ON THE CORROSION RATE OF MILD STEEL

APPENDIX D

DETAIL DISCUSSION OF THE EFFECT OF VARIOUS DETERMINANTS AND CONCENTRATIONS THEREOF ON THE CORROSION RATE OF MILD STEEL

Results are shown in Tables D1 to D4 of this Appendix and Figures 3.21 to 3.24 in paragraph 3.5.1 of the main document.

The following observations were made:

1. A linear relationship exists between corrosion rates as measured with all the different electrochemical electrode systems and conductivity and the concentration for all the chemical determinants except for hydroxide.

2. A non-linear relationship exists between the corrosion rate as measured on all the different electrochemical electrode systems and hydroxide concentration, or pH. The "corrosion rate" increased markedly from pH 10 to 13.

3. All the Tafel Plots for the "corrosion rate measurements" with the Calo.RE for CO_3^{2-} showed passivation, see Table D1. Tafel Plots produced at various hydroxide concentrations were normal except at pH 12 and 13 for which the Tafel Plots also showed passivation. See reason to follow.

4. In the case of the PVC.Carb.RE normal Tafel Plots were produced except for the sample containing 10 mg/ℓ CO_3^{2-} for which passivation occurred (Table D2). The Tafel Plots for hydroxide were all normal except at pH 12 which showed partly passivation and at pH 13, showing complete passivation.

5. The "corrosion rates" observed for samples that showed passivation at all CO_3^{2-} concentrations with the Calo.RE were much higher than the same samples showing no passivation with the PVC.Carb.RE. The same applies for hydroxide.

   Passivation occurring in the presence of CO_3^{2-}, as measured with the Calo.RE can be explained as follows. All the samples had an initial pH 12 with a [OH] of 0,01 mol/ℓ and the highest CO_3^{2-} concentration of 0,008 mol/ℓ. Under these conditions the hydroxide would promote the formation of tertiary corrosion products, FeO from $Fe(0H)_2$ and Fe_20_3 from $Fe(OH)_3$ and siderite, $FeCO_3$, causing passivation to occur fast. (Appendix A par. 1.4.1 (iv) and 1.5.1). Passivation may occur, especially if uncorroded areas still exist on the metal surface. The latter observation and the following explanation may probably explain why the corrosion rates for the PVC.Carb.RE (Table D2) are lower than for the Calo.RE (Table D1). It may be that no uncorroded areas existed on the metal surface of the PVC.Carb.RE and for this reason the corrosion process would have been much slower and therefore passivation would take longer to occur. Another explanation for these tendencies may be as follows. The influence of CO_3^{2-} on the corrosion rate, relative to the influence of the other determinants, is shown more clearly by the results in Tables D2 and D3 obtained with the PVC.Carb.RE and the corrater.

From the results obtained with the corrater (Table D3), it can be seen that the corrosion rates for CO_3^{2-} is higher than for the other determinants probably caused by the contribution of OH^- ions because the pH for CO_3^{2-} is higher than for the other determinants. Using the PVC.Carb.RE the OH^- ions had no effect on corrosion rates if one compares the corrosion rates for CO_3^{2-} with that obtained with OH^- at pH 12. The exception being for the samples with lowest CO_3^{2-} dosage for which a very high corrosion rate were obtained. In the latter case passivation occurred as can be seen in Table D2. From the latter observation it seems as if the carbonate ions act as an inhibitor by eliminating the effect of OH^-.

From the discussion above it follows that the effect of CO_3^{2-} on the corrosion rate is complicated by the presence of hydroxide ions at pH 12 and probably also by the different working electrode types used.

NB. "Corrosion rates": If passivation occurred, the high corrosion rates obtained on the anodic Tafel Slopes, were actually not corrosion rates but an indication of increasing tendencies for passivation. See 3.5.1 of main document.

TABLE D1:

CORROSION RATES MEASURED WITH CALO.RE FOR VARYING ANION CONCENTRATIONS AND pH 10

Determinants	Anion concentrations as mg/ℓ					
	10	40	80	160	320	480,0
	Corrosion rate in μm/y					
$C\ell^-$	244	343	475	874	1374	1191
SO_4^{2-}	157	279	414	676	1105	1674
NO_3^-	201	305	315	495	831	975
HCO_3^-* as mg/ℓ$CaCO_3$	83	156	292	572	742	1300
CO_3^{2-}# as mg/ℓ $CaCO_3$	1350	4220	5250	4380	3320	8130

* pH = 8,3

\# pH = 12,0

CORROSION RATES FOR INCREASING pH

pH	8	9	10	11	12	13
mol/ℓ OH^-	1×10^{-6}	1×10^{-6}	1×10^{-4}	1×10^{-3}	1×10^{-2}	1×10^{-1}
μm/y	179	122	68	304	2550	12730

TYPICAL TAFEL PLOTS FOR INCREASING CO_3^{2-} AND OH^- CONCENTRATION

mg/ℓ CO_3^{2-}	10	40	80	160	320	480
Tafel Plot	pas	pas	pas	pas	pas	pas
mol/ℓ OH^-	1×10^{-6}	1×10^{-6}	1×10^{-4}	1×10^{-3}	1×10^{-2}	1×10^{-1}
Tafel Plot	Normal	Normal	Normal	Normal	Normal	Normal

pas = Tafel Plot indicate passivation

Normal = Tafel Plot indicate no passivation

TABLE D2:

CORROSION RATES MEASURED WITH PVC.CARB.RE FOR VARYING ANION

CONCENTRATIONS AND pH 10

Determinants	Anion concentrations as mg/ℓ					
	10	40	80	160	320	480,0
	Corrosion rate in μm/y					
$C\ell^-$	218	495	681	1000	1316	1600
SO_4^{2-}	132	556	699	904	1443	1590
NO_3^-	320	429	495	704	965	1240
HCO_3^-* as mg/ℓ$CaCO_3$	91	163	295	460	714	1250
CO_3^{2-}# as mg/ℓ $CaCO_3$	858	288	160	170	151	162

* pH = 8,3
\# pH = 12,0

CORROSION RATES FOR INCREASING pH

pH	8	9	10	11	12	13
mol/ℓ OH^-	1×10^{-6}	1×10^{-6}	1×10^{-4}	1×10^{-3}	1×10^{-2}	1×10^{-1}
μm/y	109	91	20,3	213	498	1010

TYPICAL TAFEL PLOTS FOR INCREASING CO_3^{2-} AND OH^- CONCENTRATION

mg/ℓ CO_3^{2-}	10	40	80	160	320	480
Tafel Plot	pas	Normal	Normal	Normal	Normal	Normal
mol/ℓ OH^-	1×10^{-6}	1×10^{-6}	1×10^{-4}	1×10^{-3}	1×10^{-2}	1×10^{-1}
Tafel Plot	Normal	Normal	Normal	Normal	Partly pas	pas

pas = Tafel Plot indicate passivation
Normal = Tafel Plot indicate no passivation

TABLE D3:

CORROSION RATES MEASURED WITH CORRATER FOR VARYING ANION CONCENTRATIONS AND pH 10

Determinants	Anion concentrations as mg/ℓ					
	10	40	80	160	320	480
	Corrosion rate in μm/y					
$C\ell_3^-$	31	41	58	91	122	137
SO_4^{2-}	56	71	81	102	142	152
NO_3^-	51	61	66	81	107	132
HCO_3^- * as mg/ℓ$CaCO_3$	38	71	96	137	168	229
CO_3^{2-} # as mg/ℓ $CaCO_3$	305	292	310	305	305	318

* pH = 8,3

pH = 12,0

CORROSION RATES FOR INCREASING pH

pH	8	9	10	11	12	13
mol/ℓ OH^-	1×10^{-6}	1×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-2}	1×10^{-1}
μm/y	43	31	25	81	102	254

TABLE D4:

CONDUCTIVITY VERSUS VARIOUS ANION CONCENTRATIONS AT pH 10 AND HYDROXIDE FOR VARIOUS pH

Determinants	Anion concentration as mg/ℓ					
	10	40	80	160	320	480
	Conductivity in mS/m					
$C\ell^-$	3,4	15,0	25,0	50,0	95,0	140,0
SO_4^{2-}	3,7	17,0	26,0	39,0	68,0	100,0
NO_3^-	7,0	11,0	19,0	31,0	53,0	132,0
HCO_3^- * as mg/ℓ$CaCO_3$	4,4	7,7	15,5	29,0	53,0	80,0
CO_3^{2-} # as mg/ℓ $CaCO_3$	460,0	520,0	500,0	450,0	470,0	480,0

* pH = 8,3

pH = 12,0

CONDUCTIVITY FOR INCREASING pH

pH	8	9	10	11	12	13
mol/ℓ OH^-	1×10^{-6}	1×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-2}	1×10^{-1}
mS/m	3,5	6,9	4,1	25,0	270,0	2200,0

APPENDIX E

A PROPOSED COMPOSITION OF POTABLE WATER WITH LOW CORROSIVENESS

APPENDIX E

A PROPOSED COMPOSITION OF POTABLE WATER WITH LOW CORROSIVITY POTENTIAL PROPERTIES

The determination of the composition of water with good corrosion protection properties are based on the investigation of the effect of alkalinity in the six pipe system, paragraph 4.1.1.

From the graphical representation of the different indices values versus CCPP, Figures 4.6 to 4.13 of main document, the CCPP value for each index above for which non-corrosive conditions prevailed, were obtained. From the intersect of these CCPP values and the best linear fitting for CCPP $\geq$ 0 of all the other parameters the x-ordinates values were obtained as standards (see Figures 4.1 to 4.5). For corrosion rates and conductivity the smallest values, and for CCPP, calcium, Ct and alkalinity, the largest values were chosen as standards (See Table E1). All the chemical analyses of values of indices and corrosion rate results for each water sample were compared against these standards. Each sample for which a parameter confirmed to these standards, one mark was awarded. The marks for each parameter for each sample were added and the chemical analysis for those samples with total marks from 12 to 16 were chosen as water with good non-corrosive properties. Chemical analyses of eight of these samples are shown in Table E2a (set one and set two). Calculated indices making use of symbols, see Appendix G and computer printout No. 2, are shown in Table E2b, set one and set two. LSI and RSI values were determined with the Caldwell-Lawrence diagrams, Table E2c, set one and set two.

From the results in Table E2b, set one and set two, it can be seen that the symbols awarded to the indices indicated non-corrosive water for LSI, RCI, LI and CI indices. The DFI and $CaCO_3$-SS indicated scale forming properties and the RSI and LSI indices indicated non-scale forming properties. The Caldwell-Lawrence diagrams indicated over saturation for most of the samples with the LSI, but corrosive water with the RCI. Only two samples seem to be slightly aggressive with the AI index. The Y index classifies all the water samples as being intermediate corrosive. In conclusion it seems that all the indices except the RCI indicated that these water samples were non-corrosive.

The LSI and RSI values determined with the Caldwell-Lawrence diagrams are illustrated by the following example. Caldwell-Lawrence diagrams for two different conditions were used, one for an ionic strength (μ) of 0,0025 and a temperature of 20°C and one for an ionic strength (μ) of 0,0050 and a temperature of 25°C. For each set of analyses, Table E2, an intercept for calcium content as $CaCO_3$ and alkalinity at the saturation points were found on the two diagrams. The pH values read from the diagrams at the intersects of the two lines are equal to pHs. The mean value for the two pHs values were calculated and from these values the LSI and RCI values were determined.

Example based on chemical analyses of water sample after eight days exposure, from Table E2.

- Langelier

  Si = pH - pHs
  pHs is the pH where the alkalinity and Ca lines intersect, thus

  Si = 8,5 - 8,39 = +0,11
  Si = 8,5 - 8,33 = +0,17
  Mean value is 0,14 >-0,5 indicating the water as non-corrosive.

- Ryznar

  RI = 2pHs - pH
  = 16,8 - 8,5 = +8,3
  = 16,7 - 8,5 = +8,2
  Mean value of +8,3 and +8,2 is +8,25 > + 7,0 indicating the water is under saturated and corrosive.

These results correspond with those obtained from the graphical representation of the Langelier and Ryznar values as a function of CCPP. In all these cases the Langelier Index indicated water with good protection against corrosion while the Ryznar Index indicated corrosive water.

- CCPP for water sample on day eight as determined with the Caldwell-Lawrence diagrams

  The envelope formed by the alkalinity, Ca (as $CaCO_3$) and pH lines indicated over saturated water with a CCPP of 2,23 that corresponded favourably with the calculated CCPP value of 2,34.

It thus follows that the Ryznar Index is fallible because it predicted water that is under saturated. Results from the Langelier Index on the other hand corresponds with the results obtained from the Caldwell-Lawrence diagrams.

TABLE E1 STANDARD VALUES OBTAINED FROM SUPERIMPOSING GRAPHS OF INDICES ON ALL OTHER PARAMETERS OBTAINED FOR DIFFERENT CCPP VALUES

a) MEASURED CORROSION RATES IN μm/y

Indices	CCPP ≤	Coupons ≤	Corrater ≤	ECI-Calo.RE ≤	ECI-Carb.PVC.RE ≤	ECI-Carb.RE ≤
DFI	1,0	152	109	61	51	229
LSI	0,0	173	109	61	58	267
LI	2,5	140	107	58	43	165
RCI	0,0	198	109	61	58	167
AI	2,0	152	104	58	46	178
Y	1,0	152	109	61	51	228
Chosen values*	1,0	140	104	58	43	165

*Values chosen as standards

b) CALCULATED CORROSION RATES IN μm/y

Indices	CCPP ≥	CR_{prog} ≤	CR_{cond} ≤	CR_{TDS} ≤
DFI	1,0	264	192	188
LSI	0,0	267	196	193
LI	2,5	259	191	185
RCI	0,0	267	196	191
AI	2,0	259	191	188
Y	1,0	259	191	185
Chosen values*	1,0	259	191	185

*Values chosen as standards

c) ANALYSES

Indices	CCPP ≥	Conductivity mS/m ≤	Calcium mg/ℓ ≥	C_t mg/ℓ as $CaCO_3$ ≥	Alkalinity mg/ℓ as $CaCO_3$ ≥
DFI	1,0	15,3	16,3	73	72
LSI	0,0	15,0	16,6	73	75
LI	2,5	15,4	16,4	72	72
RCI	0,0	15,3	16,4	72	72
AI	2,0	15,3	16,3	72	72
Y	1,0	15,3	16,3	73	72
Chosen value*	1,0	15,0	16,4	73	75

*Values chosen as standards

The Casil Index was not considered because it gave scattered results
The Ryznar Index is not applicable because it indicated corrosive water for all CCPP values up to 19 mg/ℓ $CaCO_3$ which was out of the range for the graphs.

Values chosen as standards were:

Smallest positive value for CCPP
Smallest value for corrosion rates
Smallest value for conductivity
Largest value for calcium
Largest value for C_t and
Largest value for alkalinity

DFI : Drinving Force Index
LSI : Langelier Saturation Index
LI : Larson Index
RCI : Riddick Corrosion Index
AI : Aggressive Index
Y : Feigenbaum, Gal-OR, Yahalom Index

TABLE E2: PROPERTIES OF WATER WITH LOW CORROSIVENESS

a) CHEMICAL ANAYSES (SET ONE)

ANALYSES	Pipe Number			
	4	3	3	4
	Exposure time in days			
	8	2	8	7
	Points score for each sample			
	16	14	14	13
Conductivity mS/m	14,5	17,3	15,3	17,0
pH	8,5	8,3	8,6	8,5
TDS mg/ℓ	97	116	103	114
Alkalinity as mg/ℓ $CaCO_3$	71	89	81	73
Hardness as mg/ℓ $CaCO_3$	66	68	60	73
Calcium mg/ℓ	22	23	19	25
Magnesium mg/ℓ	2,70	2,60	3,0	2,6
Sodium mg/ℓ	4,4	10,0	12,0	3,9
Iron mg/ℓ (before contact)#	0,19	0,61	0,41	0,05
Activated SiO_2 mg/ℓ	9,0	9,3	9,6	6,7
Total SiO_2 mg/ℓ	9,0	9,8	9,6	9,4
Ammonia mg/ℓ	0,05	0,05	0,05	0,05
Nitrite-N mg/ℓ	0,30	0,30	0,30	0,30
Nitrate-N mg/ℓ	0,30	0,23	0,12	0,25
Sulphate mg/ℓ	5,0	5,0	5,0	5,0
Chloride mg/ℓ	5,0	5,0	5,0	5,0
*CCPP	2,3	2,5	3,5	2,9

*CCPP calculated with JTG computer program
#Before contact with metal

TABLE E2: PROPERTIES OF WATER WITH LOW CORROSIVENESS

b) CHEMICAL ANAYSES (SET TWO)

ANALYSES	Pipe Number			
	6	6	6	6
	Exposure time in days			
	8	7	6	5
	Points score for each sample			
	13	12	12	12
Conductivity mS/m	15,5	15,5	15,3	15,3
pH	8,5	8,4	8,3	8,3
TDS mg/ℓ	104	104	103	103
Alkalinity as mg/ℓ $CaCO_3$	75	74	73	73
Hardness as mg/ℓ $CaCO_3$	74	72	69	69
Calcium mg/ℓ	24	24	23	23
Magnesium mg/ℓ	3,4	2,9	2,8	2,9
Sodium mg/ℓ	5,3	3,8	4,3	4,7
Iron mg/ℓ (before contact)#	0,10	0,07	0,24	0,25
Activated SiO_2 mg/ℓ	7,8	7,10	7,5	4,0
Total SiO_2 mg/ℓ	10,0	10,0	10,0	10,0
Ammonia mg/ℓ	0,05	0,05	0,05	0,05
Nitrite-N mg/ℓ	0,3	0,3	0,3	0,3
Nitrate-N mg/ℓ	0,69	0,11	0,12	0,13
Sulphate mg/ℓ	5,0	5,0	5,0	5,0
Chloride mg/ℓ	5,0	5,0	5,0	5,0
*CCPP	3,3	2,5	1,7	1,6

*CCPP calculated with JTG computer program
#Before contact with metal

TABLE E2: PROPERTIES OF WATER WITH LOW CORROSIVENESS

a) CHEMICAL ANALYSES

ANALYSES	RANGE
Conductivity mS/m	14,5 - 17,0
pH	8,3 - 8,6
TDS mg/ℓ	97,4 - 116
Alkalinity as mg/ℓ $CaCO_3$	71 - 89
Hardness ag mg/ℓ $CaCO_3$	69 - 73
Calcium mg/ℓ	19 - 25
Magnesium mg/ℓ	2,6 - 3,4
Sodium mg/ℓ	3,9 - 10,0
Iron mg/ℓ (before contact with metal)	0,05 - 0,61
Activated SiO_2 mg/ℓ	4,0 - 9,6
Total SiO_2 mg/ℓ	9,0 - 10,0
Ammonia mg/ℓ	<0,05
Nitrite-N mg/ℓ	<0,30
Nitrate-N mg/ℓ	0,11 - 0,69
Sulphate mg/ℓ	<5
Chloride mg/ℓ	<5

TABLE E2: PROPERTIES OF WATER WITH LOW CORROSIVENESS

b) INDICES VALUES PRESENTED AS SYMBOLS (SET 1)

INDICES	Pipe Number			
	4	3	3	4
RSI	-S	-S	-S	-S
LSIc	-C	-C	-C	-C
AI	-A	-A	-A	-A
DFI	+S	+S	+S	+S
RCIc	-C	-C	-C	-C
LI	-C	-C	-C	-C
Y	+C(2)	+C(2)	+C(2)	+C(2)
CI	-C	-C	-C	-C
$CaCO_3$-SS	+S	+S	+S	+S

b) INDICES VALUES PRESENTED AS SYMBOLS (SET 2)

INDICES	Pipe Number			
	4	3	3	4
RSI	-S	-S	-S	-S
LSIc	-C	-C	-C	-C
AI	-A	-A	+A(1)*	+A(1)*
DFI	+S	+S	+S	+S
RCIc	-C	-C	-C	-C
LI	-C	-C	-C	-C
Y	+C(2)	+C(2)	+C(2)**	+C(2)**
CI	-C	-C	-C	-C
$CaCO_3$-SS	+S	+S	+S	+S

+A(1)* - Slightly aggresive
+C(2)** - Intermediate corrosive

Values and indications in Table E2(b) for respectively set 1 and 2 to be read in conjunction with values in Table E2 (c) set 1 and 2.

TABLE E2 PROPERTIES OF WATER WITH LOW CORROSIVENESS

c) RCI AND LSI AS DETERMINED WITH CALDWELL LAWRENCE DIAGRAMS (SET 1)

Indices	Pipe Number			
	4	3	3	4
RCI	8,25	8,13	8,26	8,05
LSI	0,14	0,09	0,21	0,23

c) RCI AND LSI AS DETERMINED WITH CALDWELL LAWRENCE DIAGRAMS (SET 2)

Indices	Pipe Number			
	6	6	6	6
RCI	8,09	8,17	8,28	8,28
LSI	0,21	0,11	0,01	0,01

APPENDIX F

PROPOSED EQUATIONS FOR CALCULATING THE CORROSION RATE OF MILD STEEL AND AN EVALUATION THEREOF

APPENDIX F

PROPOSED EQUATIONS FOR CALCULATING THE CORROSION RATE OF MILD STEEL IN WATER WITH KNOWN CHEMICAL COMPOSITION.

Three empirical equations for calculating the expected corrosion rate of mild steel were developed by Rand Water. The first and second equations were based on the linear relationships obtained between the measured corrosion rates and TDS/conductivity and can be written as,

$$\text{CRm} = 1{,}9\ \text{TDS} - 3{,}84 \quad \text{(F4)}$$

for total dissolved solids (TDS) and,

$$\text{CRm} = 12{,}9\ \text{mS/m} - 4{,}74 \quad \text{(F5)}$$

for conductivity (mS/m)

The third equation, in which the effect of different chemical and physical factors were combined, is as follows,

$$\text{CRm} = [4{,}09\ Cl^- + 4{,}0\ SO_4^{2-} + 2{,}79\ Cl_2 + 9{,}78\ NO_3^- - N + 3{,}12\ \{\text{Talk} - \text{CCPP/F1}\} + 9{,}98\ \text{pH} - 118] \times F1 \times F2 \quad \text{(F6)}$$

The third equation (F6) can be obtained by combining the linear equations developed for different determinants. See equations 4 to 7 and 15 from paragraph 3.5.1 in the main report.

Cl^- : $CR = 3{,}20\ Ce + 253$ .... (4)
SO_4^{2-} : $CR = 3{,}15\ Cs + 147$ .... (5)
NO_3^- : $CR = 1{,}70\ Cn + 212$ .... (6)
HCO_3^- as $CaCO_3$ (Talk): $CR = 2{,}44\ Ch + 79{,}5$ .... (7)
Cl_2 paragraph 3.5.3 : $CR = 5{,}465\ Cc + 55{,}1$ .... (15)

and other factors like CCPP, dissolved oxygen, from paragraph 3.5.4 and temperature, paragraph 3.5.5, of the form;

$$CR = [3{,}2\ Cl^- + 3{,}15\ SO_4^{2-} + 5{,}47\ Cl_2 + 1{,}70\ NO_3^- + 2{,}44\ \{\text{Talk} - \text{CCPP}/F_1\} + 249^*] \times F_1 \times F_2 \quad \text{(F1)}$$

$$F_1 = 0{,}12\ (\%O_2) + 124$$

$$F_2 = 2{,}6\ (t) + 58{,}4$$

with Cl^-, SO_4^{2-}, Cl_2, NO_3^- in mg/ℓ, Talk and CCPP in mg $CaCO_3$, DO in % dissolved oxygen and t in °C

REMARKS CONCERNING EQUATION (F1)

1. *249 is the average for all the intercepts of the above linear equation excluding F_1 and F_2.

2. At pH 8,3; Talk represented the total carbonate as bicarbonate in the solution, while CCPP represented the fraction of the total carbonate concentration removed from the solution as precipitated $CaCO_3$.

3. Where chlorine is added to water half of the chlorine will hydrolyze to hypochlorous acid/hypochlorite ions and half will appear as hydrochloric acid. The ratio of hypochlorous acid to hypochlorite ions depends on the pH of the water. For this reason the effect of chloride on the corrosion of mild steel need to be investigated further.

4. CCPP is divided by F_1, because, in the determination of CCPP the effect of temperature is already built in.

FIRST EVALUATION OF EQUATION (F1)

For all the different water types on which the research was done, the terms for chlorine was ignored, because the samples did not contain any chlorine. The oxygen and temperature factors had a value of one because all the samples were saturated with oxygen and the temperature kept at 22°C.

Three Sterkfontein Dam water samples were investigated. See analysis in Tables F1 for the mean of the analyses. The CCPP was calculated with the Stasoft (Friend, 1992) and JTG programs. Results are shown in Table F2.

If the CCPP values are negative, it has to be added to the Talk in the corrosion equation. The measured and calculated corrosion rates are shown in Table F3 and it can be seen that the calculated corrosion rates are much higher than the measured corrosion rates. If the CCPP values are ignored when negative the calculated and measured corrosion rates compare more rationally, see Table F4, but the calculated values are still much higher than the measured values. Another possibility is to ignore the sulphate content, because it may precipitate as calcium sulphate.

From the conductivity and equations, $\mu = 1{,}68 \times 10^{-4}$ mS/m and $\mu = 2{,}5 \times 10^{-5}$ TDS, it follows that the TDS for one samples was 62,00 mg/l. From a material balance it follows that,

Ca^{2+} = 8,4 mg/l = 28,98 $CaSO_4$
Mg^{2+} = 2,7 mg/l = 16,40 $Mg(HCO_3)_2$
Na^+ = 4,7 mg/l = 3,99 2,16 $NaHCO_3$ + 1,83 Na_2SO_4
K^+ = 1,3 mg/l = $\underline{2{,}895}$ k_2SO_4
Total 52,265
+ SiO_2 = $\underline{8{,}800}$
Total TDS = 61,065

The total TDS is 61,065 mg/l

The TDS calculated from the conductivity and the TDS calculated through a material balance, is approximately the same and therefore the sulphate in the samples would be in the dissolved form and can not be ignored in the corrosion equation.

The only other term in the equation that needs to be addressed, is the mean value for the intercepts of equations 4 - 7 and 15. These intercepts were obtained by extrapolating the straight lines to the zero concentrations of the chemical investigated. This intercept must therefore be equal to the corrosion rates of deionized water at the pH of the samples. It was found, however, that the corrosion rates in deionized water at pH 8,3, were much lower (±20,32 μm/y) that the corrosion rates obtained from the intercepts.

By replacing the constant 249* with the corrosiveness of deionized water at the pH of Sterkfontein Dam water, namely 9,5, the calculated corrosion rates corresponded more favourably with the measured corrosion rates as shown in Table F5. The constant 249* was thus replaced by a term D, where D is the corrosion rate for deionized water at the pH of the water investigated.

The presence of activated silica in the samples, may cause the corrosion rates measured to be lower than the corrosion rates calculated, because of its possible inhibitory qualities.

SECOND EVALUATION OF EQUATION (F1)

Six samples were prepared with laboratory chemicals with chemical composition as shown in Table F6. The first three samples contained no sulphate and the second three samples contained sulphate. Important to note is that the CCPP was negative for all these samples.

Comparison of the measured and calculated corrosion rates, ignoring the negative CCPP values, are shown in Table F7.

It is again noted that the corrosiveness increases with increasing TDS and will for this reason also increase with conductivity. The corrosiveness is also higher for the samples containing sulphate than for those samples without sulphate, because the added sulphate increases the conductivity. In all cases the calculated corrosion rates compared favourably with the measured corrosion rates. The corrosion rate for deionized water at pH 8,3 was ± 21,0 μm/y.

Analysis of the same samples containing sulphate but at a pH 10 are shown in Table F8. The higher pH resulted in a positive CCPP for all the samples and were therefore subtracted from the Talk in the equation. For pH 10 the corrosiveness of deionized water is 35,56 μm/y which will become the term D in the equation. The measured and calculated corrosion rates are shown in Table F9. Although the measured corrosion rates were higher than the calculated corrosion rates at the initial stage it was about the same as the calculated corrosion rates after two days. This tendency was caused by the formation of precipitated $CaCO_3$ (not on the working electrode, but on the bottom of the container) causing a decrease in the conductivity and therefore a decrease in the corrosion rates. The corrosion rates after two days were also lower for the samples at pH 10 than at pH 8,3, (compare results in Tables F7 and F9) caused by the precipitation of calcium carbonate at pH 10.

THIRD EVALUATION OF EQUATION (F1)

Five Sterkfontein Dam water samples were dosed with respectively 10, 20, 30, 40 and 50 mg/l $CaCO_3$. The analysis and CCPP values are shown in Table F10.

A comparison of the measured and calculated values are shown in Table F11 and graphically represented in figures F1 and F2.

The same tendency was observe, namely that the corrosion rate increases as the conductivity increases (Table F11 and Figure F3) because of an increase in the Talk and/or the TDS of the samples caused by the addition of $CaCO_3$.

REMARKS CONCERNING THE CORROSION EQUATION (F1)

1. *The effect of chlorine on corrosion can probably be solved as follows:*

   If chlorine (Cl_2) is dosed half of it will become hydrochloric acid by way of the reaction.

   $Cl_2 + H_20 \rightarrow HOCl + HCl$ ....(a)

   At pH = 9,5, the pH at which the investigation was done, the right hand side of the reaction will become,

   $$\begin{matrix} Na^+ & + & Na^+ \\ OCl^- & & Cl^- \end{matrix} \qquad \text{..................(b)}$$

   For chlorine (Cl_2) dosed the corrosion equation found was,

   $CR = 5{,}47\ Cl_2 + 55{,}1$ ....(c)

   For chloride (Cl^- or NaCl) dosed the corrosion equation found was,

   $CR = 3{,}20\ Cl + 253$ ....(d)

   The term 5,47 Cl_2 in equation (c) can now be written as,

   $5{,}47\ (0{,}5\ C\ell_2 + 3{,}2 \times 0{,}5\ C\ell_2)$ ....(e)

   with the term 0,5 $C\ell_2$ in brackets, representing the hypochlorite ion, and the term 3,2 x 0,5 $C\ell_2$, representing the chloride contribution to the corrosion rate, see reaction (a) and (b). Because the chloride contribution to the corrosion rate will be picked up in the chloride analysis the second term in brackets can be ignored. Equation (e) will than become 5,47 x 0,5 x $C\ell_2$ or 2,74 x $C\ell_2$.

The intercepts of equation (c) and (d) were ignored for the reason discussed elsewhere. At the pH of normal potable water about 80% of the chlorine compounds known as free available chlorine will be present as hypochloric ions. Hypochloric ions probably increase the conductivity and thus cause an increase in the corrosiveness of water. The term 2,74 $C\ell_2$ multiplied by 0,80 would thus become 2,19 $C\ell_2$.

2. *Because of the fact that nitrates are usually analysed as mg/l nitrate-nitrogen* (NO_3-N) the factor 1,7 multiplied by the nitrate concentration is now also multiplied by 4,5 so as to change it to NO_3^-. The factor now becomes 7,65.

3. The term D in the equation which is directly proportional to the corrosion rate of deionized water at the pH of the sample can be replaced by the equation,

   $D = 7{,}81\ pH - 43$

   This equation derives from the corrosion rates measured for deionized water at different pH values as shown in Table F12. The relationship between pH and corrosion rates is linear with a correlation coefficient of 0,997.

The corrosion equation will now become

$$CR = [3{,}2\ Cl^- + 3{,}15\ SO_4^{2-} + 2{,}19\ Cl_2 + 7{,}65\ NO_3\text{-}N + 2{,}44\ \{Talk - CCPP/F_1\} + 7{,}81\ pH - 43] \times F_1 \times F_2 \quad \text{(F2)}$$

EQUATIONS BASED ON TDS AND CONDUCTIVITY AND A POSSIBLE FURTHER REFINEMENT OF THE CORROSION EQUATION(F2)

In Table F13 the results of the foregoing investigations are summarised for increasing measured corrosion rates, corresponding TDS and conductivity. The results are also graphically represented in Figures F4, F5 and F6. In Figure F4 the measured corrosion rates versus the calculated corrosion rates are shown, in Figure F6 the measured corrosion rates versus conductivity and in Figure F5 the measured corrosion rates versus TDS are shown. Linear relationships can now be obtained for,

- measured corrosion rates versus calculated corrosion rates.
  $CRm = 1{,}278\ CRcal - 64$ . . . . (F3)
  Correlation coefficient (r) = 0,961

- measured corrosion rates versus total dissolved solids (TDS)

CRm = 1,9 TDS - 3,84 . . . . (F4)

Correlation coefficient (r) = 0,960

- measured corrosion rates versus conductivity (mS/m)

CRm = 12,9 mS/m - 4,74 . . . . (F5)

Correlation coefficient (r) = 0,962

By replacing the CRcal in equation (F3) with the calculated valued from equation (F2) the corrosion rate equation will now become,

CRm = 1,278 [equation (F2)] - 64

Thus

$$CRm = [4{,}09\ Cl^- + 4{,}0\ SO_4^{2-} + 2{,}79\ Cl_2 + 9{,}78\ NO_3\text{-}N + 3{,}12\ \{Talk - CCPP/F_1\} + 9{,}98\ pH - 118] \times F_1 \times F_2 \quad \text{(F6)}$$

Furthermore, the corrosiveness of water can also be calculated from equations (F4) and (F5) because of the linear relationship that exist between the measured corrosion rates and TDS/ conductivity.

RELATIONSHIP BETWEEN MEASURED OR CALCULATED CORROSION RATES AND INDICES

No agreement has yet been reached on a general corrosion index that is applicable to potable water as most indices have limitations (Mullen. D *et al*, 1980). To control the inhibitor treatment the generally accepted mils per year guidelines used in the heating and cooling industries as followed by the Middlesex Water Company were adopted namely,

- <2 mils/year indicated both excellent water and pipeline protection.
- 2 - 5 mils/year indicates good water and protection.
- 5 - 10 mils/year indicates acceptable, and
- >10 mils/year indicates corrosive water.

or in micron per year the values from top to bottom will become <51, 51 - 127, 127 - 254 and > 254 μm/y.

A survey of the literature by Merrill and Sanks (James R Millette, *et al*, 1980) suggests that the characteristics of a well conditioned (over saturated) water include

1. An over saturation of $CaCO_3$, with a $CaCO_3$ precipitation potential of 4 - 10 mg/l.

2. Calcium and alkalinity values of at least 40 mg/l as $CaCO_3$, with calcium and

alkalinity present in approximately equal concentrations.

3 An alkalinity to (Cl^- + SO_4^{2-}) ratio of at least 5:1 with all concentrations expressed as $CaCO_3$.

4 pH *in the range* 6,8 - 7,3

It is not always possible to prepare water that will adhere to all four above conditions. Conditions 1, 2 and 3 are the most important and should be preserved. Condition 4 can only be preserved when the untreated water is initially high in calcium and alkalinity.

The analysis of Sterkfontein Dam water was used as a basis to determine the relationship between the calculated corrosion rates and the indices making use of the above mentioned conditions. CCPP values of 4 to 10 could not be obtained (first condition) without altering the pH (fourth condition). With the Stasoft programme the mg/l NaOH dosage to obtained CCPP of 4 and 10 was computed as an example giving a pH of 9,07 and 9,43 for the two waters. The alkalinity to (Cl^- + SO_4^{2-}) ratio, (third condition) is about 5:1. The alkalinity was somewhat higher than 40 mg/l because of the NaOH added and the calcium content as calcium carbonate was 40 mg/l. The indices were calculated with a computer program developed by the Rand Water and the results are shown in Tables F14(a) and (b) for CCPP 4 and 10 before $CaCO_3$ precipitation and Tables F15(a) and (b) after $CaCO_3$ precipitation. All the indices except the Ryznar Index indicated that the waters before $CaCO_3$ precipitation is oversaturated, non-aggressive and non-corrosive. The Feigenbaum Index although not applicable, indicated that the water is slightly corrosive. After $CaCO_3$ precipitation only three indices namely the Riddic, Larson and Casil Indices indicated non-corrosion conditions while all the other indices indicated it to be corrosive.

The corrosion rates calculated with equations (F3), (F4) and (F5) are shown in Table F16 for CCPP values of 4 and 10. Comparison of these calculated corrosion rates with the Middlesex Water Company's index indicated good water and protection (51 - 127 μm/year) to water of acceptable quality (127 - 254 μm/year). The results obtained with the developed equations compared favourably with the results obtained with most of the calculated indices.

A computer program was developed whereby the CCPP could be calculated, making use of Joint Task Group program method (Merril, 1990). In the computer program the effect of negative CCPP values were taken into consideration because it can be assumed that the precipitated calcium carbonate that can dissolve will always be available in mild steel pipelines. The program will predict the corrosiveness of the water before and after calcium carbonate precipitated for positive CCPP values and before and after calcium carbonate dissolved for negative CCPP values. For positive CCPP values the TDS and conductivity of the water will decrease with calcium carbonate precipitation and therefore the corrosiveness of the water will decrease. For negative CCPP values the TDS and conductivity will increase after the precipitated calcium carbonate has dissolved, thus the corrosiveness of the water will increase. The program not only predicts the alkalinity and pH but also the TDS and conductivity of the water at equilibrium.

If the computer program is not available the corrosiveness of the water can be determined by making use of the worksheet and a laboratory method for determining CCPP as shown in Addendum H.

Physical conditions for which the corrosion equations can be applied are:

- initial corrosiveness of potable water
- uniformly corroded mild steel

- if the analysis of those components that appear in the equations are known, namely conductivity, TDS, chloride, sulphate, chlorine, nitrate-N, Talk (before and after "marble" test), CCPP, pH, temperature and oxygen content
- pH 6,5 - pH 10
- microbiologically corrosion being absent

TABLE F1 STERKFONTEIN DAM WATER

PARAMETERS	ANALYSIS
Conductivity mS/m	9,00
Turbidity NTU	1,90
pH	6,66
pHs	8,96
Dissolved solids mg/ℓ	62,00
Alkalinity as mg $CaCO_3$/ℓ	29,00
Hardness $CaCO_3$/ℓ	26,00
Calcium mg/ℓ	8,4
Magnesium mg/ℓ	2,7
Sodium mg/ℓ	4,7
Potasium mg/ℓ	1,3
Active SiO_2 mg/ℓ	8,8
Total SiO_2 mg/ℓ	12,00
Nitrite mg/ℓ N	0,15
Nitrate mg/ℓ	0,15
Sulphate mg/ℓ	23,00
Chloride mg/ℓ	<10

TABLE F2

CCPP VALUES FOR THREE STERKFONTEIN DAM SAMPLES

SAMPLE	CCPP (STASOFT)	CCPP (J.T. GROUP)
1	-22,9	-31,12
2	-24,9	-35,85
3	-23,9	-33,10

TABLE F3

COMPARISON OF MEASURED AND CALCULATED CORROSION RATES (μm/y). NEGATIVE CCPP ADDED TO TALK.

SAMPLE	μm/y MEASURED	μm/y CALCULATED
1	114	363
2	119	358
3	127	373

TABLE F4

COMPARISON OF MEASURED AND CALCULATED CORROSION RATES (μm/y). NEGATIVE CCPP VALUES IGNORED.

SAMPLE	μm/y MEASURED	μm/y CALCULATED
1	114	307
2	119	297
3	127	315

TABLE F5

COMPARISON OF MEASURED AND CALCULATED CORROSION RATES (μM/Y). REPLACING MEAN INTERSEPT (5,9 μm/y) WITH CORROSION RATE DIONISED DAM WATER AT pH 6,6

SAMPLE	μm/y MEASURED	μm/y CALCULATED
1	114	165
2	119	160
3	127	175

TABLE F6

ANALYSES ON SIX WATER SAMPLES PREPARED IN THE LABORATORY WITH LABORATORY (AR) REAGENTS AT pH 8,3.

	SAMPLE 1	SAMPLE 2	SAMPLE 3
pH	8,3	8,30	8,3
Cl^- mg/ℓ	10,00	5,00	100,00
Ca^{2+} mg/ℓ	10,00	50,00	20,00
Talk mg $CaC0_3$/ℓ	40,08	20,11	50,12
Na^+ mg/ℓ	24,88	12,44	87,84
NO_3^- mg/ℓ	31,00	155,00	62,00
TDS mg/ℓ	99,87	234,44	299,84
CCPP mg $CaCO_3$/ℓ	-3,43	-1,04	-2,04
Temperature °C	22	22	22
Calculated corrosion rate μm/y	206	357	849
Measured corrosion rate μm/y	201	445	531

	SAMPLE 4	SAMPLE 5	SAMPLE 6
pH	8,3	8,3	8,3
Cl^- mg/ℓ	10,00	5,00	100,00
Ca^{2+} mg/ℓ	10,00	50,00	20,00
Talk mg $CaC0_3$/ℓ	40,99	20,11	50,12
Na^+ mg/ℓ	31,88	18,94	94,34
NO_3^- mg/ℓ	31,00	155,00	62,00
SO_4^{2-} mg/ℓ	20,00	20,00	20,00
TDS mg/ℓ	129,57	264,00	329,44
CCPP mg $CaCO_3$/ℓ	-3,60	-1,07	-2,10
Temperature °C	22	22	22
Calculated corrosion rate μm/y	270	414	632
Measured corrosion rate	282	533	752

TABLE F7

COMPARISON OF MEASURED AND CALCULATED CORROSION RATES FOR SIX LABORATORY PREPARED SAMPLES AT pH 8,3

SAMPLE	CALCULATED CR μm/y	MEASURED CR μm/y
1	206	201
2	351	445
3	849	531
4	270	282
5	414	533
6	632	752

TABLE F8

ANALYSIS OF LABORATORY PREPARED SAMPLES AT pH 10.

		SAMPLE 7	SAMPLE 8	SAMPLE 9
pH		10,00	10,00	10,00
Cl^- mg/ℓ		10,00	5,00	100,00
Ca^{2+} mg/ℓ		10,00	50,00	20,00
Talk mg $CaCO_3$/ℓ		41,8	24,84	51,91
Na^+ mg/ℓ		31,88	18,94	94,34
NO_3^- mg/ℓ		31,00	155,00	62,00
SO_4^{2-} mg/ℓ		20,00	20,00	20,00
TDS mg/ℓ		129,57	264,00	329,00
CCPP mg $CaC0_3$/ℓ		15,90	18,51	28,90
Temperature °C		22	22	22
Calculated corrosion rate μm/y		246	394	528
Measured corrosion rate μm/y	After 24h	302	510	893
	After 48h	229	429	691

TABLE F9

COMPARISON OF MEASURED AND CALCULATED CORROSION RATES FOR LABORATORY PREPARED SAMPLES AT pH 10.

SAMPLE	CALCULATED CR µm/y	MEASURED CR µm/y	
7	246	302*	229**
8	394	510*	429**
9	528	893*	691**

* after one day after preparation

** after two days after preparation.

TABLE F10

ANALYSIS OF STERKFONTEIN DAM WATER DOSED WITH INCREASING CALCIUM BICARBONATE AS mg $CaCO_3/\ell$.

mg $CaCO_3/\ell$	10	20	30	40	50
pH	6,6	6,7	6,8	6,8	6,8
mS/m	7,4	8,0	8,7	9,4	10,1
TDS mg/ℓ	81	91	101	111	121
Cl^- mg/ℓ	-	-	-	-	-
SO_4^{2-} mg/ℓ	21	21	21	21	21
Talk mg $CaCO_3/\ell$	22,87	27,20	29,58	34,11	46,0
Ca^{2+} mg/ℓ	12,5	16,5	20,5	24,8	28,5
NO_3^- mg/ℓ	1,02	1,02	1,02	1,02	1,02
CCPP mg $CaCO_3/\ell$	-26,9	-24,8	-26,4	-27,7	-24,8

TABLE F11

COMPARISON OF MEASURED AND CALCULATED CORROSION RATES FOR STERKFONTEIN DAM WATER DOSED WITH CALCIUM BICARBONATE AS mg $CaCO_3/\ell$.

mg $CaCO_3/\ell$	10	20	30	40	50
Measured CR μm/y	109	117	127	140	157
Calculated CR μm/y	132	145	150	161	191
Conductivity mS/m	7,4	8,0	8,65	9,47	10,1

TABLE F12

CORROSION RATE VERSUS pH USING DIONISED WATER SATURATED WITH OXYGEN.

pH	CORROSION RATES IN μm/y D
6,6	9,5
8,3	21
9,2	29
10,0	36

TABLE 13 RELATIONSHIP BETWEEN MEASURED AND CALCULATED CORROSION RATES AND CORRESPONDING TDS AND CONDUCTIVITY

Sample	Measured μm/y	Calculated μm/y	TDS mg/ℓ	Conductivity mS/m
Sterkfontein 4	109	132	50,00	7,40
Sterkfontein 1	114	165	61,00	9,00
Sterkfontein 2	119	160	61,00	9,00
Sterkfontein 3	127	175	62,00	9,00
Sterkfontein 5	117	145	54,00	8,00
Sterkfontein 6	127	150	59,00	8,70
Sterkfontein 7	140	161	60,30	9,40
Sterkfontein 8	157	191	68,00	10,10
Solution 1	201	203	108,00	16,00
Solution 7	229	246	130,00	19,50
B4 Water after chlorination	259	253	148,00	22,00
Mabopane	269	301	175,00	26,00
ModderBee	276	243	161,00	24,00
Zuurbekom	279	320	168,00	25,00
Solution 4	292	270	131,00	19,50
A12 Water after chlorination	284	293	175,00	26,00
Leeupoort	285	264	168,00	25,00
Rustenburg	290	262	168,00	25,00
Palmiet	293	288	161,00	24,00
Klipbank	297	262	195,00	29,00
Alrode	305	269	181,00	27,00
Sandton	309	293	175,00	26,00
Maple	316	297	161,00	24,00
Krugersdorp	318	305	175,00	26,00
Sasol	318	328	188,00	28,00
Eikenhof	320	323	161,00	24,00

TABLE 13 Continue

Pelindaba	330	305	175,00	26,00
Deelkraal	343	345	202,00	30,00
Libanon	353	340	208,00	31,00
Vaaldam 0.4	358	277	181,00	27,00
Vaaldam 0.2	365	296	188,00	28,00
Vaaldam 0.8	367	316	181,00	27,00
Vaaldam 0.0	376	333	181,00	27,00
Vaaldam 0.6	376	318	181,00	27,00
Vaaldam 1.0	379	320	181,00	27,00
Solution 8	427	394	229,00	34,00
Solution 2	445	351	228,00	34,00
Solution 3	531	570	327,00	48,00
Solution 5	533	414	235,00	35,00
Solution 9	691		336,00	50,00
Solution 6	752		343,00	51,00

TABLE F14(a) CORROSIVE INDICES - CALCULATED VALUES FROM DETERMINANTS RESULTS ON WATER SAMPLES : WELL-CONDITIONED WATER

DATE: 11/08/92

1. DATA

Ca = Alk (40 mg/ℓ $CaCO_3$)
NaOH for pH 9,07
CCPP = 4
pH = 9,07

Analysis	Reading
Conductivity (mS/m)	10,63
Turbidity (NTU)	3,8
pH	9,07
Suspended solids (mg/l)	8
Dissolved solids (mg/l)	71,45
Alkalinity (mg $CaCO_3$/l)	53,1
Hardness (mg $CaCO_3$/l)	51,81
Calcium (mg/l)	16
Magnesium (mg/l)	2,6
Sodium (mg/l)	4,5
Potassium (mg/l)	1,3
Iron (mg/l)	0,16
Aluminium (mg/l)	0,1
Ammonium (mg N/l)	0,1
Nitrite (mg N/l)	0,05
Nitrate (mg N/l)	0,18
Sulphate (mg/l)	3,84
Chloride (mg/l)	2,84
DOC (mg/l)	0,1
Dissolved Oxygen (mg/l)	6,9
Saturated Oxygen (mg/l)	6,9
Temperature (C)	23
Zink (mg/l)	0,1
Manganese (mg/l)	0,1
SiO_2 Total (mg/l)	16
SiO_2 Active (mg/l)	12
Free CO_2 (mg/l)	0,079801
Max. Mg $CaCO_3$/l Dissolved	1.3E+01

2. CALCULATED VALUE

Ion Strn.	1,79E-03
Alkalinity	53,1
Acidity	46,58122
Ct	49,84061

Index	Value
pHs	8,834480
RSI	8,598960
LSI	0,235519
AI	12,39715
DFI	3,118260
RCI	4,405685
LI	0.2
YI	583,2182
CI	0,597587

$CaCO_3$-ss	27,17233

3. WATER CONDITIONS

Index	Symbol
RSI s	-S
LSI s	+S
LSI c	-C
AI a	-A
DFI s	+S
RCI c	-C
LI c	-C
YI s/c	+C(1) N/A
CI c	-C

$CaCO_3$ - ss	+S

TABLE F14(b) CORROSIVE INDICES - CALCULATED VALUES FROM DETERMINANTS RESULTS ON WATER SAMPLES : WELL-CONDITIONED WATER

DATE: 11/08/92

1. DATA

Ca = Alk (40 mg/ℓ CaCO$_3$)
NaOH for pH 9,43
CCPP = 1-
pH = 9,43

2. CALCULATED VALUE

Ion Strn.	1,85E-03
Alkalinity	56,4
Acidity	42,11512
Ct	49,25756

Analysis	Reading
Conductivity (mS/m)	11
Turbidity (NTU)	3,8
pH	9,43
Suspended solids (mg/l)	8
Dissolved solids (mg/l)	74,1
Alkalinity (mg CaCO$_3$/l)	56,4
Hardness (mg CaCO$_3$/l)	51,81
Calcium (mg/l)	16
Magnesium (mg/l)	2,6
Sodium (mg/l)	4,5
Potassium (mg/l)	1,3
Iron (mg/l)	0,16
Aluminium (mg/l)	0,1
Ammonium (mg N/l)	0,1
Nitrite (mg N/l)	0,05
Nitrate (mg N/l)	0,18
Sulphate (mg/l)	3,84
Chloride (mg/l)	2,84
DOC (mg/l)	0,1
Dissolved Oxygen (mg/l)	6,9
Saturated Oxygen (mg/l)	6,9
Temperature (C)	23
Zink (mg/l)	0,1
Manganese (mg/l)	0,1
SiO$_2$ Total (mg/l)	16
SiO$_2$ Active (mg/l)	12
Free CO$_2$ (mg/l)	0,032079
Max. Mg CaCO$_3$/l Dissolved	6,1E+00

Index	Value
pHs	8,810375
RSI	8,190751
LSI	0,619624
AI	12,78333
DFI	6,556846
RCI	2,327913
LI	0.2
YI	1206,814
CI	0,567678

CaCO$_3$-ss	33,89950

3. WATER CONDITIONS

Index	Symbol
RSI s	-S
LSI s	+S
LSI c	-C
AI a	-A
DFI s	+S
RCI c	-C
LI c	-C
YI s/c	+C(1) N/A
CI c	-C

CaCO$_3$ - ss	+S

TABLE F15(a) CORROSIVE INDICES - CALCULATED VALUES FROM DETERMINANTS RESULTS ON WATER SAMPLES : WELL-CONDITIONED WATER

DATE: 11/08/92

1. DATA

Ca = Alk (40 mg/ℓ $CaCO_3$)
NaOH for pH 9,07
CCPP = 4
pH = 8,23 *at Equilibrium*

Analysis	Reading
Conductivity (mS/m)	9,85
Turbidity (NTU)	3,8
pH	8,23
Suspended solids (mg/l)	8
Dissolved solids (mg/l)	66,21
Alkalinity (mg $CaCO_3$/l)	47,85
Hardness (mg $CaCO_3$/l)	46,58
Calcium (mg/l)	13,9
Magnesium (mg/l)	2,6
Sodium (mg/l)	4,5
Potassium (mg/l)	1,3
Iron (mg/l)	0,16
Aluminium (mg/l)	0,1
Ammonium (mg N/l)	0,1
Nitrite (mg N/l)	0,05
Nitrate (mg N/l)	0,18
Sulphate (mg/l)	3,84
Chloride (mg/l)	2,84
DOC (mg/l)	0,1
Dissolved Oxygen (mg/l)	6,9
Saturated Oxygen (mg/l)	6,9
Temperature (C)	22
Zink (mg/l)	0,1
Manganese (mg/l)	0,1
SiO_2 Total (mg/l)	16
SiO_2 Active (mg/l)	12
Free CO_2 (mg/l)	0,560916
Max. Mg $CaCO_3$/l Dissolved	9,2E+01

2. CALCULATED VALUE

Ion Strn.	1,66E-03
Alkalinity	47,85
Acidity	48,18814
Ct	48,01907

Index	Value
pHs	8,961686
RSI	9,693372
LSI	-0,73168
AI	11,45083
DFI	0,376012
RCI	5,509627
LI	0.2
YI	91,06276
CI	0,543008

$CaCO_3$-ss	-57,6670

3. WATER CONDITIONS

Index	Symbol
RSI s	-S
LSI s	-S
LSI c	+C
AI a	+A(1)
DFI s	-S
RCI c	-C
LI c	-C
YI s/c	+C(3) N/A
CI c	-C

$CaCO_3$ - ss	-S

TABLE F15(b) CORROSIVE INDICES - CALCULATED VALUES FROM DETERMINANTS RESULTS ON WATER SAMPLES : WELL-CONDITIONED WATER

DATE: 11/08/92

1. DATA

Ca = Alk (40 mg/ℓ $CaCO_3$)
NaOH for pH 9,43
CCPP = 10
pH = 8,33 at Equilibrium

Analysis	Reading
Conductivity (mS/m)	9,48
Turbidity (NTU)	3,8
pH	8,33
Suspended solids (mg/l)	8
Dissolved solids (mg/l)	63,75
Alkalinity (mg $CaCO_3$/l)	46,05
Hardness (mg $CaCO_3$/l)	41,5
Calcium (mg/l)	11,86
Magnesium (mg/l)	2,6
Sodium (mg/l)	4,5
Potassium (mg/l)	1,3
Iron (mg/l)	0,16
Aluminium (mg/l)	0,1
Ammonium (mg N/l)	0,1
Nitrite (mg N/l)	0,05
Nitrate (mg N/l)	0,18
Sulphate (mg/l)	3,84
Chloride (mg/l)	2,84
DOC (mg/l)	0,1
Dissolved Oxygen (mg/l)	6,9
Saturated Oxygen (mg/l)	6,9
Temperature (C)	22
Zink (mg/l)	0,1
Manganese (mg/l)	0,1
SiO_2 Total (mg/l)	16
SiO_2 Active (mg/l)	12
Free CO_2 (mg/l)	0,427129
Max. Mg $CaCO_3$/l Dissolved	7,6E+01

2. CALCULATED VALUE

Ion Strn.	1,59E-03
Alkalinity	46,05
Acidity	45,88624
Ct	45,96812

Index	Value
pHs	9,045338
RSI	9,760677
LSI	-0,71533
AI	11,46525
DFI	0,388473
RCI	3,396070
LI	0.2
YI	93,14089
CI	0,459092

$CaCO_3$-ss	-46,6743

3. WATER CONDITIONS

Index	Symbol
RSI s	-S
LSI s	-S
LSI c	+C
AI a	+A
DFI s	-S
RCI c	-C
LI c	-C
YI s/c	+C(3) N/A
CI c	-C

$CaCO_3$ - ss	-S

TABLE 16 CALCULATED CORROSION RATES BASED ON DIFFERENT DETERMINANTS

Sample	CR from Conductivity Equation F4	CR from Equation F5	CR from TDS Equation F6
pH = 9,07 Table 62(a) CCPP - 4	122	150	122
pH = 9,43 Table 62(b) CCPP - 10	114	140	114

Equation F4: CRrm = 3,84

Equation F5: CRrm = 12,9 mS/m - 4,74

Equation F6: CRrm = [4,09 Cl^- + 4,0 SO_4^{2-} + 2,79 Cl_2 + 9,78 NO_3^-N + 3,12 {Talk - CCPP/F1} + 9,98pH - 118] x F1 x F2.

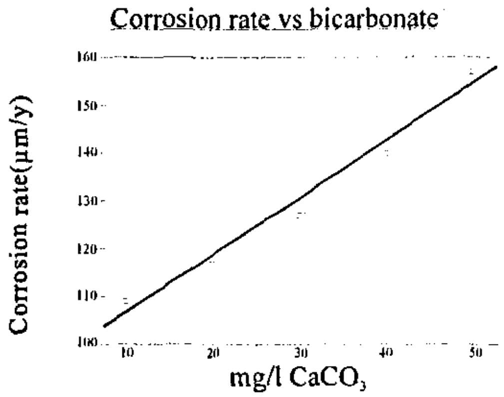


FIGURE F1

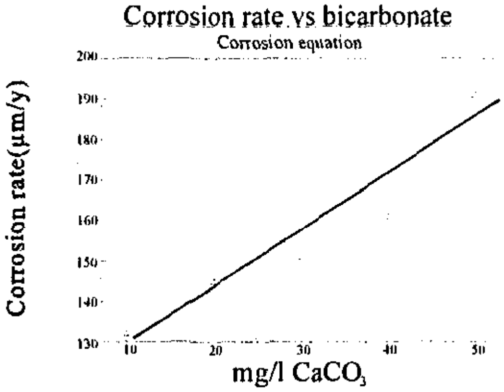


FIGURE F2

FIGURE F1 AND F2: **MEASURED r = 0,99 AND CALCULATED (r = 0,95) CORROSION RATES VERSUS INCREASING ALKALINITY**

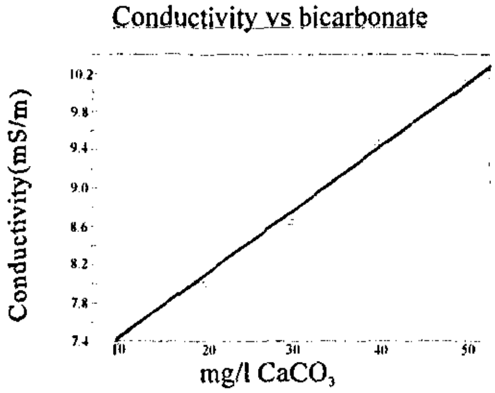


FIGURE F3

FIGURE F3: CONDUCTIVITY VERSUS INCREASING ALKALINITY (r = 1,00)

FIGURE F4

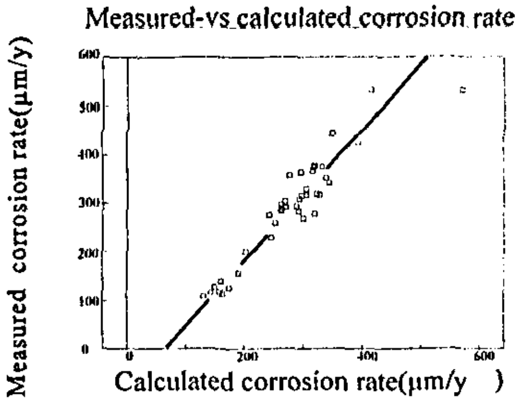


FIGURE F4: MEASURED VERSUS CALCULATED CORROSION RATE (r = 0,9)

FIGURE F5

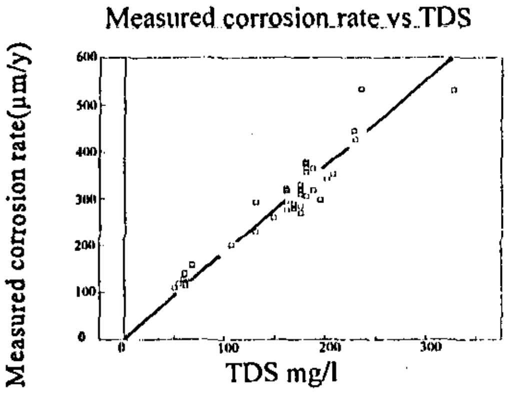


FIGURE F5: MEASURED CORROSION RATE VERSUS TDS (r = 0,96)

FIGURE F6

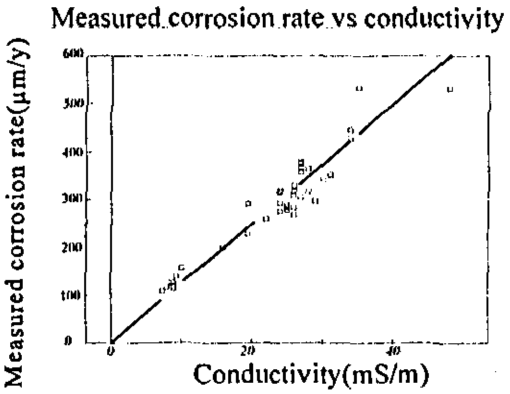


FIGURE F6: MEASURED CORROSION RATE VERSUS CONDUCTIVITY (r = 0,96)

APPENDIX G

1. COMPUTER PROGRAM FOR CALCULATING CORROSION INDICES

2. COMPUTER PROGRAM FOR CALCULATING

   - CALCIUM CARBONATE PRECIPITATION POTENTIAL AND EQUILIBRIUM ALKALINITY AND pH

   - CORROSION RATES FOR DIFFERENT EQUATIONS DEVELOPED BY RAND WATER

APPENDIX G

1. COMPUTER PROGRAM FOR CALCULATING CORROSION INDICES

The computer program for calculating the corrosion indices (Index program) was developed on a Lotus 123 worksheet from the equations for the different indices shown in Table G1. The effect of temperature on the equilibrium constants for the carbonic system and ionic strength were also taken into consideration.

1.1 PRESENTATION OF DATA AND RESULTS

Computer printout G1 (following page G6) depicts an example of the calculated values (right hand columns 2 + 3) from the data inserted in the left hand column (1).

For interpretation, the calculated corrosion indices values in column 2 should be compared to the description of the indices in Table G1 and the symbols in column 3 with computer printout G2.

The meaning of the symbols in columns 2 and 3 are as follows:

Ion strn : ionic strength (μ)
Alkalin : Total alkalinity (Talk)
Acidity : Total acidity (Tacid)
Ct : Total carbonic species
pHs : pH where calcium carbonate solubility equilibrium prevails
RSI : Ryznar stability Index
LSI : Langelier saturation Index
AI : Aggressive Index
DFI : Driving force Index (McCauley's)
RCI : Riddick Corrosive Index
LI : Larson Index
Y : Feigenbaum, Gal-or, Yahalom combination
CI : Casil Index
$CaCO_3$-SS : Calcium carbonate saturation state
RSIs : Ryznar for scale forming
LSIs : Langelier for scale forming
LSIc : Langelier for corrosion
AIa : Aggressive
DFIs : Driving force for scale forming
RCIs : Riddick corrosive for scale forming
LIc : Larson for scale forming
Ys/c : Feigenbaum, Gal-or, Yahalom for scale forming or corrosion
CIc : Casil for corrosion

1.2 EQUATIONS FOR CALCULATING INDICES USING A LOTUS 123 WORKSHEET

The following calculations were done on the appropriate data for the equations as indicated to produce the relative value in the right hand column. The meaning of some of the symbols used in the equations are explained under "Meaning of Symbols and Equations" of main document.

1.2.1 Ionic strength (μ)

Calculated from

$\mu = 2{,}5 \times 10^{-5}$ Sd

1.2.2 Alkalinity (Talk)

Determination normally done by direct analysis

1.2.3 Acidity

The acidity is calculated by equation (B15), Addendum B paragraph 3.2

1.2.4 Total carbonic concentration (Ct)

Ct is calculated by equation (B13), Addendum B paragraph 3.1

1.2.5 pHs

pHs is calculated from

$\text{pHs} = A + B - \log [Ca^{2+}] - \log [\text{Talk}]$

$A = -0{,}025t + 2{,}6$

$\log B = 3{,}5 \times 10^{-5}\ \text{Sd} + 0{,}986$ for Sd = 0 - 200 mg/ℓ

and $\log B = 3{,}2 \times 10^{-6}\ \text{Sd} + 0{,}9924$ for Sd >200 mg/ℓ

$[Ca^{++}]$ as mg $CaCO_3$/ℓ and Talk as mg $CaCO_3$/ℓ from left hand column

1.2.6 Riddick Corrosion Index (RSI)

RSI = 2pHs - pH

pHs calculated from equation for pHs, paragraph 1.2.5, above

pH by direct measurement with a pH meter

1.2.7 Langelier Saturation Index (LSI)

LSI = pH - pHs

pHs calculated from equation for pHs, paragraph 1.2.5, above

pH by direct measurement

LSIs for scale forming

LSIc for corrosion

1.2.8 Aggressive Index (AI)

AI = pH + log [(Talk) (Ca hard)]

Ca - hardness and Talk by direct analysis and expressed as mg $CaCO_3/\ell$

1.2.9 Driving Force Index (DFI)

DFI = $(Ca^{2+} \times CO_3^{2-})/K^1sol \times 10^{10}$

Ca^{2+} as mg $CaCO_3/\ell$ by direct analysis and CO_3^{2-} from equation (B10), Addendum B paragraph 2.2

1.2.10 Riddick's corrosion index (RCI)

RCI = 75/Talk [CO_2 + ½ (Thard - Talk)+C1 + 2N]
10/SiO_2 (DO +2/DOs)

N = mg NO_3^-/ℓ : mg $NO_3^-N/\ell \times 4{,}429$

C1 = mg $C\ell^-/\ell$

CO_2 from equation (B17b), Addendum B paragraph 3.4, as mg $CaCO_3/\ell$.

DO = dissolved oxygen concentration in mg/ℓ

DOS = saturated dissolved oxygen in mg/ℓ.

1.2.11 Larson Index (LI)

LI = $C\ell^- + SO_4^{2-}$/Talk

$C\ell^-$ = mg $C\ell^-/\ell$ expressed as equivalent mg $CaCO_3/\ell$

SO_4^{2-} = mg SO_4^{2-}/ℓ expressed as equivalent mg $CaCO_3/\ell$

LI = {($C\ell^-$ x 100/35,5 x 2) + (SO_4^{2-} x 100/96)}/Talk

1.2.12 Feigenbaum, Gal-or, Yahalom (Y)

$Y = A_2H + (B\,[C1^-] + [SO_4^{2-}])\exp(-1/A_2H) + C_1$

$A_2 = 3{,}5 \times 10^{-4}$

$B = 0{,}34$

$H = (Ca^{2+})(HCO_3^-)^2/(CO_2)$ from

$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3(S) + CO_2 + H_2O$

$C_1 = 19$

A, B and C are constants supplied by the author

$[Ca^{2+}]$, $[C\ell^-]$, $[SO_4^{2-}]$ en $[CO_2]$ in mg/ℓ

$[HCO_3^-]$ as mg $CaCO_3/\ell$ from equation (B9), Addendum B paragraph 2.1;

$[HCO_3^-] \times fm \times 10^5$

$[CO_2]$ as mg CO_2/ℓ from equation (B17a), Addendum B paragraph 3.4;

$[CO_2] \times 4{,}4 \times 10^4$

1.2.13 Casil Index (CI)

CI = Ca + Mg + $HSiO_3$ - anions/2

Ca, Mg, $HSiO_3$ and anions in meq/ℓ

Cations

Ca^{2+} in mg/ℓ x 1/40/2 = mg Ca^{2+}/ℓ x 0,05 = meq Ca^{2+}/ℓ

Mg^{2+} in mg/ℓ x 1/24,3/2 = mg Mg^{2+}/ℓ x 0,0823 = meq Mg^{2+}/ℓ

SiO_2 in mg/ℓ x 77,1/60 = mg $HSiO_3^-$ x 1/77,1/1 = mg SiO_2/ℓ x 0,0167

= meq SiO_2/ℓ

Anions

meg HCO_3^-/ℓ from eq (B9), Addendum B paragraph 2.1, x 10^3

meg CO_3^{2-}/ℓ from eq (B10), Addendum B paragraph 2.2, x 10^3

mg $NO_2.N/\ell$ x 46/14 = mg NO_2^-/ℓ x 1/46/1 = mg $NO_2.N/\ell$ x 0,0714

= meq NO_2^-/ℓ

mg $NO_3.N/\ell$ x 62/14 = mg NO_3^-/ℓ x 1/62/1 = mg $NO_3.N/\ell$ x 0,0714

= meq NO_3^-/ℓ

mg SO_4^{2-}/ℓ x 1/96/2 = mg SO_4^{2-}/ℓ x 0,0208 = meq SO_4^{2-}/ℓ

mg $C1/\ell$ x 1/35,5/1 = mg $C\ell/\ell$ x 0,0282 = meq $C\ell/\ell$

meg $OH^- = [\{(10^{pH-pKw})/fm\} - 10^{-pH}]$ x 10^3

TABLE G1 INTERPRETATION OF INDICES OF THE POTENTIAL CORROSIVITY OF WATER

INDEX	INTERPRETATION
Langelier (LSI) pH - pHs	>0: Water is supersaturated; tends to precipitate $CaCO_3$
LSIs	=0: In equilibrium; $CaCO_3$ scale is neither dissolved nor deposited <0: Water is undersaturated; dissolves solid $CaCO_3$
LSIc	>-0,5: Corrosion free for cold water >0,0: Corrosion free for hot water
Aggressive Index (AI) pH + log [(Talk) (Ca hardness)]	<10: Very aggressive 10-12: Moderately aggressive >12: Non-aggressive
Ryznar Stability Index (RSI) 2pHs - pH	<6,5: Water supersaturated; tends to precipitate $CaCO_3$ 6,5 <RSI<7,0: In equilibrium; $CaCO_3$ scale is neither dissolved nor deposited >7,0: Water is undersaturated; tends to dissolve solid $CaCO_3$
Riddick Corrosion Index (RCI) $\frac{75}{\mathrm{Talk}} [CO_2 + \frac{1}{2}(\mathrm{Thard}-\mathrm{Talk}) + \mathrm{C1} + 2\mathrm{N}] \mathrm{X} \frac{10}{SiO_2} \mathrm{X} \frac{\mathrm{DO}+2}{\mathrm{DOv}}$	0-5 Scale forming 6-25 Non corrosive 26-50 Moderately corrosive 51-75 Corrosive 75 - 100 Very corrosive 101+ Extremely corrosive
Driving Force Index (DFI) Ca^{2+} x $CO^{2-}{}_3/K_{sol}$ x 10^{10}	>1: Water supersaturated; tends to precipitate $CaCO_3$ 1: In equilibrium; $CaCO_3$ scale is neither dissolved not deposited <1: Water undersaturated; tends to dissolve $CaCO_3$
Larson Index (LI) $Cl^- + SO_4^{2-}/\mathrm{Talk}$	>0,5: Possibility of corrosive action exists
Casil Index (CI) $Ca + Mg + HSiO_3 - \frac{\mathrm{anions}}{2}$	<0: Very corrosive water 0,0 - 0,1: Slightly corrosive >0,1: Non corrosive
Feigenbaum, Gal-or, Yahalom (FGY) $Y = A_2 H + B[(Cl^-) + (SO_4^{2-})]\exp(-1/A_2H) + C_1$	Y <200: Highly corrosive Y 250-500: Intermediate corrosion Y >500: Little corrosion

COMPUTER PRINTOUT G1

RAND WATER

CORROSIVE INDICES – CALCULATED VALUES FROM DETERMINANTS
RESULTS ON WATER SAMPLES : STERKFONTEIN

DATE : 13/03/91

1. DATA

ALKALINITY
pH = 7.6
OXYGEN = 98%
0 mg/l NaOH

2. CALCULATED VALUE

Ion Strn.	3.54E–03
Alkalin.	89
Acidity	98.50985
Ct	93.75492

ANALYSIS	R'DING
Conductivity (mS/m)	12
Turbidity (nTU)	10
pH	7.6
Suspended Solids (mg/l)	10
Dissolved Solids (mg/l)	141.6
Alkalinity (mg CaCO3/l)	89
Hardness (mg CaCO3/l)	26
Calcium (mg/l)	6.6
Magnesium (mg/l)	2.4
Sodium (mg/l)	28.4
Potassium (mg/l)	4.5
Iron (mg/l)	0.15
Aluminium (mg/l)	0.23
Ammonium (mg N/l)	0.05
Nitrite (mg N/l)	0.05
Nitrate (mg N/l)	0.6
Sulphate (mg/l)	6
Chloride (mg/l)	5
DOC (mg/l)	1.7
Dissolved Oxygen (mg/l)	6.9
Saturated Oxygen (mg/l)	6.9
Temperature (C)	23
Zink (mg/l)	0.05
Manganese (mg/l)	0.05
SiO2 Total (mg/l)	17
SiO2 Active (mg/l)	7.4
Free CO2 (mg/l)	4.367386
Max. mg CaCO3/l Dissolved	2.2E+02

INDEX	VALUE
pHs	9.049973
RSI	10.49994
LSI	–1.44997
AI	10.76687
DFI	0.075222
RCI	–10.7530
LI	0.2
YI	37.05762
CI	–0.39493

CaCO3–ss	–202.849

3. WATER CONDITIONS.

INDEX	SYMBOL	
RSI s	–S	
LSI s	–S	
LSI c	+C	
AI a	+A(1)	
DFI s	–S	
RCI c	–C	
LI c	–C	
YI s/c	+C(3)	N/A
CI c	+C(3)	

CaCO3–ss	–S

COMPUTER PRINTOUT G2

KEY TO CORROSIVE INDICES

Meaning	Symbol
Not Scale-forming	-S
Equilibrium	EQ
Scale-forming	+S
Non-Corrosive	-C
Corrosive	+C
Little or Slightly Corrosive	+C(1)
Intermediately Corrosive	+C(2)
High or Very Corrosive	+C(3)
Not Aggressive	-A
Little or Slightly Aggressive	+A(1)
High or Very Aggressive	+A(3)
Saturation State	ss
Not Applicable	N/A

2. COMPUTER PROGRAM CORRATE BAS 3.51 FOR CALCULATING:

- Calcium Carbonate Precipitation Potential and equilibrium alkalinity and pH.
- Corrosion rates for different equations developed by Rand Water.

CORRATE ver 3.41 USER'S MANUAL

ABOUT CORRATE

Corrate ver 3.41 originally started out as a method to determine the Calcium Carbonate Precipitate Potential (read as CCPP), and was originally written for the Joint Task Group. Thereafter, it was decided to introduce more functions into the program, including the ability to calculate the corrosion rate of mild steel for a water sample's analyses. This led to the birth of **COR**rosion **RATE**, a program which is used by Rand Water's Experimental Water Purification Plant to calculate these aforementioned results.

CORRATE was written in Turbo Basic, and the source code (CORRATE.BAS) - listed in Appendix B - is 22530 bytes long. To make matters easier for the user, this code was compiled to an executable file, hence CORRATE.EXE (at 67585 bytes). All point-and-shoot menus and pop-up windows were created with the aid of TBMENU.INC and TBWINDO.INC respectively.

INSTALLATION ON DRIVE C

CORRATE is distributed on a DSDD 5.25" floppy disk. To run the program, simply type

A:CORRATE followed by <CR>

Similarly, installation on the computer's hard drive is as easy. In DOS, change to the directory you wish to install CORRATE.EXE in, and type

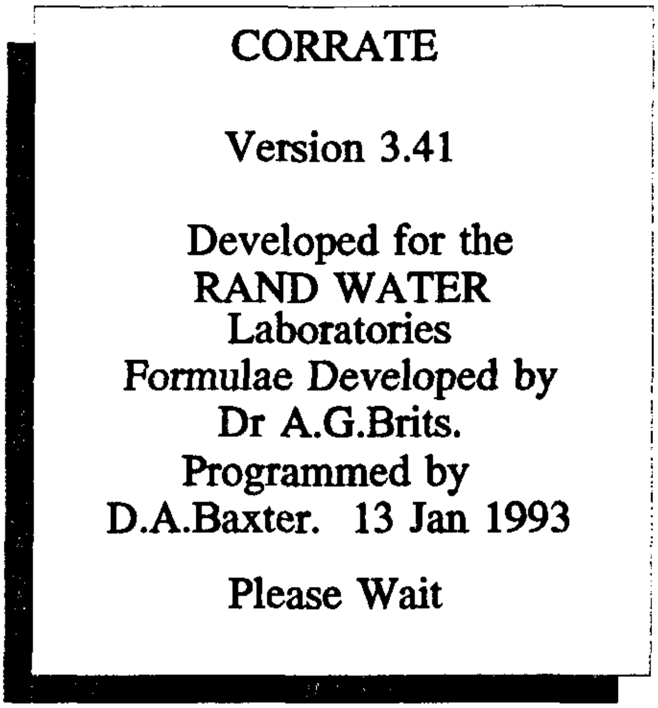
COPY A:\CORRATE.EXE followed by <CR>

Then, to run CORRATE on the hard drive, change to the directory in which the program was installed, and type

CORRATE followed by <CR>

RUNNING CORRATE

After typing CORRATE at the prompt, a screen similar to the following will appear :-



CORRATE

Version 3.41

Developed for the
RAND WATER
Laboratories
Formulae Developed by
Dr A.G.Brits.
Programmed by
D.A.Baxter. 13 Jan 1993

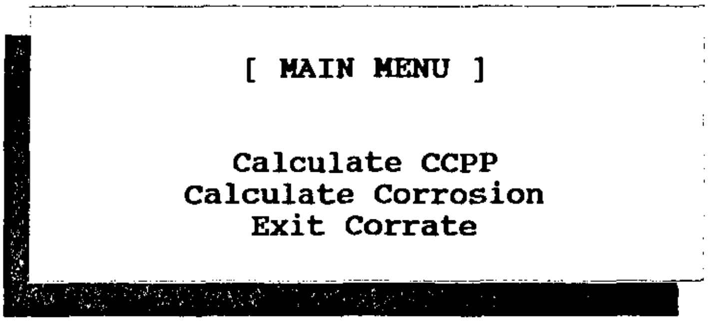
Please Wait

Please note that this welcome message will remain on your screen for 5 seconds irrespective of whether you press <CR>, Spacebar, <ESC>, etc, so please do not press anything on your keyboard whilst this screen is active.

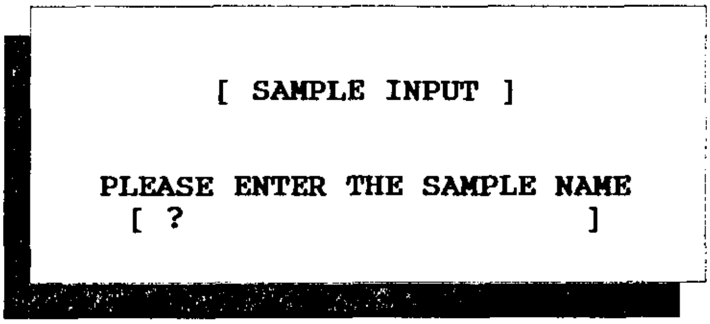
After 5 seconds have passed, a point-and-shoot Main Menu screen appears. Operation of this menu is very simple -

- use the arrow keys to highlight your choice
- press <CR>

Follows is an approximation of the appearance of this Main Menu screen.



Normally, the first choice would then be to highlight **Calculate CCPP**, and press <CR>. Once you have accomplished this, a screen prompting the user for the sample's name will appear. This screen is only for heading purposes, so type in the name of your choice, followed by <CR>. This screen appears as follows.



PLEASE ENTER THE SAMPLE NAME
[?]

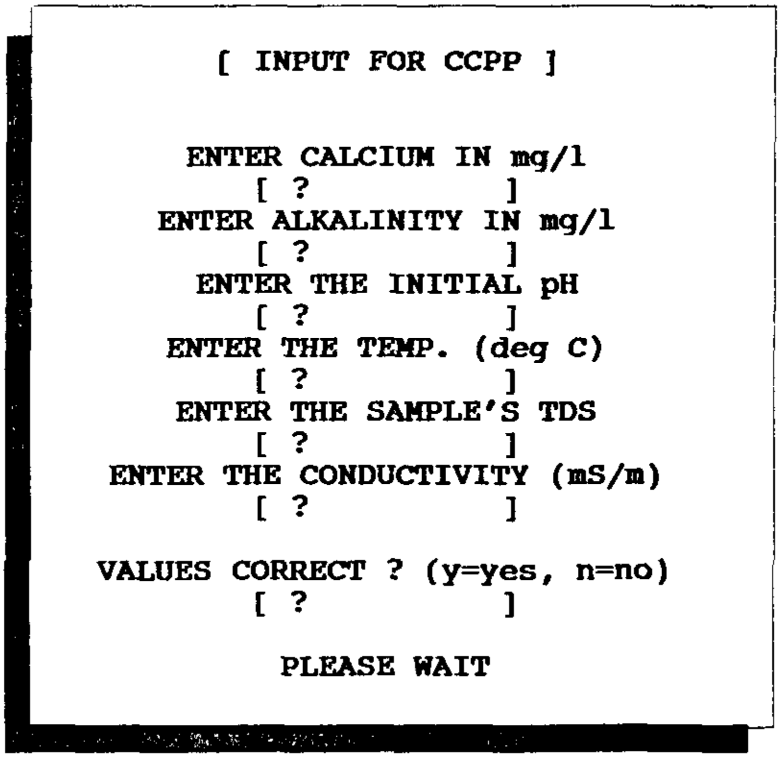
The next step in the program now appears on the screen. This involves the entering of the data required by the CORRATE program to enable the calculation of the CCPP value for your sample. Data required is as follows -

- Calcium (in mg/l)
- Alkalinity (in mg/l as $CaCO_3$)
- pH of the sample
- Temperature of the sample (in deg.C)
- TDS of the sample
- Conductivity of the sample (in mS/m)

Once again, to enter these values, simply type in the value corresponding to each parameter, and press <CR>. The program will then automatically move to the next input point. After all the data has been entered, the program queries whether the above data is correct or not. This can be answered by either

- n or N for NO, whereupon you shall repeat the above data input, or
- y or Y for YES, on which the program continues to the following step, namely calculating the CCPP value. A **PLEASE WAIT** message will appear on the screen to indicate that the calculation is in process. Please do not use the keyboard until the next screen appears.

An approximation of the input screen for CCPP calculation is as follows.

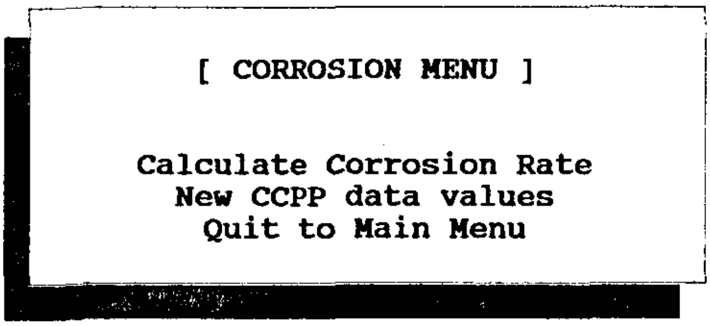


```
          [ INPUT FOR CCPP ]


        ENTER CALCIUM IN mg/l
            [ ?          ]
      ENTER ALKALINITY IN mg/l
            [ ?          ]
         ENTER THE INITIAL pH
            [ ?          ]
       ENTER THE TEMP. (deg C)
            [ ?          ]
       ENTER THE SAMPLE'S TDS
            [ ?          ]
  ENTER THE CONDUCTIVITY (mS/m)
            [ ?          ]

VALUES CORRECT ? (y=yes, n=no)
            [ ?          ]

             PLEASE WAIT
```

Now that the CCPP has been calculated by CORRATE, a screen displaying the results appears. A prompt at the bottom of the window will query as to whether you require a printout of these results or not. Once again, this can be answered in one of two ways -

- n or N for NO, in which case you will be returned to the Main Menu, or
- y or Y for YES. Then a **"Printing, Please Wait..."** prompt will appear, during which time you are Please not to use the keyboard at all. Once printing has ceased, you will be returned to the Main Menu.
  NOTE: ENSURE THAT YOUR PRINTER IS CONNECTED, IS ON, AND THAT IT HAS PAPER BEFORE YOU PRESS y OR Y.

Normally, the next step in running the program is to calculate that sample's Corrosion Rate. This is done by highlighting the **Calculate Corrosion** option, and pressing <CR>. A Corrosion Menu screen, working on the same principle as the previous menu, will now appear, similar to the following.



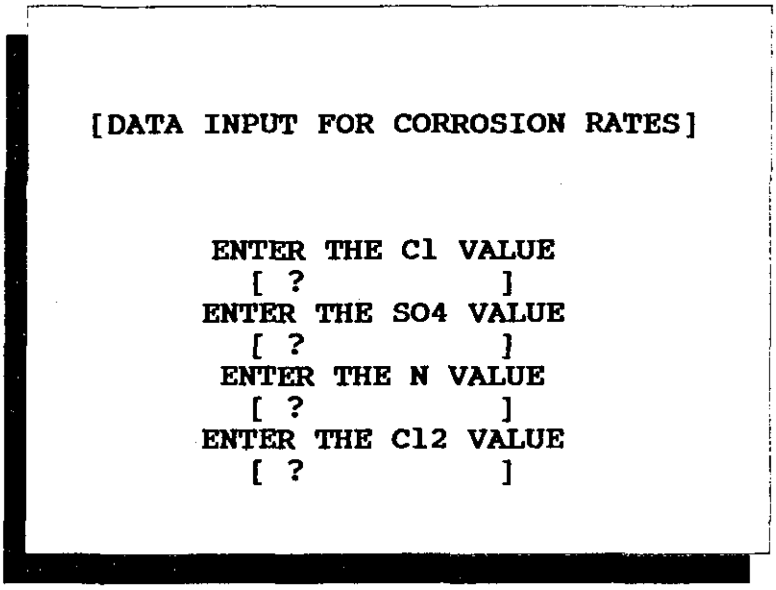
To now calculate the corrosion rate of the sample, simply

- highlight **Calculate Corrosion Rate**
- press <CR>

This option allows you to calculate the corrosion rate of the sample that you calculated the CCPP value of earlier. A new screen now appears, and encompasses the input data required to calculate the corrosion rate. This data includes

- Cl value (mg/l)
- SO_4value (mg/l)
- N value (mg/l) - the program coverts this to NO_4
- Cl_2 value (mg/l)

This screen is similar to the following.

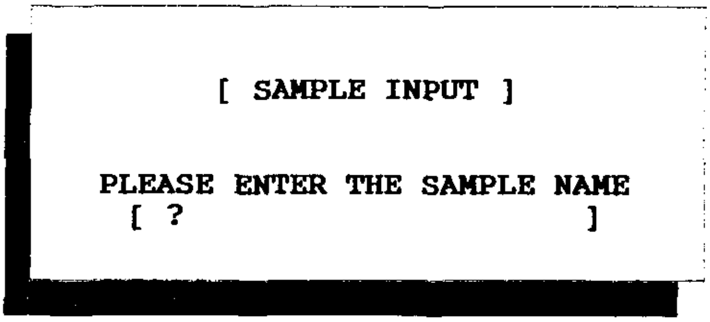


```
[DATA INPUT FOR CORROSION RATES]


       ENTER THE Cl VALUE
          [ ?        ]
       ENTER THE SO4 VALUE
          [ ?        ]
        ENTER THE N VALUE
          [ ?        ]
       ENTER THE Cl2 VALUE
          [ ?        ]
```

As with the previous data entry screens, simply type the value corresponding with the parameter into the space provided. Once input is completed, a results screen will appear. At the bottom of the window of this screen, the program prompts the user whether he would like a printout or not. This can be answered by one of the following,

- n or N for NO, and the program will return to the Corrosion Menu, or
- y or Y for YES. A "**Printing, Please Wait...**" prompt will appear. Please do not use the keyboard until printing has ceased. The program then returns control to the Corrosion Menu.
  NOTE: ENSURE THAT YOUR PRINTER IS CONNECTED, IS ON, AND THAT IT HAS PAPER BEFORE YOU PRESS y OR Y.

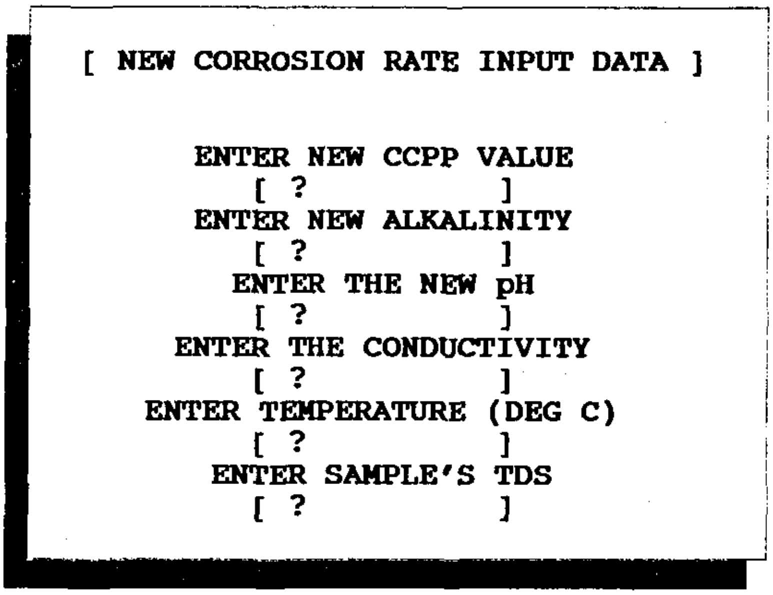
Now you have successfully completed calculating the CCPP and Corrosion Rates for a set of data. You could either highlight the **Quit to Main Menu**, and press <CR> to return to the Main Menu, or you could highlight **New CCPP data values**, and press <CR>. This option allows the user to calculate the corrosion rate for a sample with custom data values. What it basically does, is to overwrite the previous CCPP, Alkalinity, Conductivity, Temperature and TDS values from the previous sample with the user's custom data. The following screen now appears.



```
[ SAMPLE INPUT ]

PLEASE ENTER THE SAMPLE NAME
 [ ?                        ]
```

This is a screen to prompt the user for a new name for the sample data to be entered. Once again, it is purely for heading purposes and can be treated exactly as the previous one.

The next input window is a screen for the input data of that sample, and can be treated as with all the other previously. It approximately appears as follows.



```
[ NEW CORROSION RATE INPUT DATA ]


      ENTER NEW CCPP VALUE
         [ ?          ]
      ENTER NEW ALKALINITY
         [ ?          ]
        ENTER THE NEW pH
         [ ?          ]
     ENTER THE CONDUCTIVITY
         [ ?          ]
   ENTER TEMPERATURE (DEG C)
         [ ?          ]
       ENTER SAMPLE'S TDS
         [ ?          ]
```

After the data has been captured, the program returns control to the **CORROSION MENU**, whereupon the user can highlight the Calculate Corrosion Rate option and go through the corresponding steps.

To quit the CORRATE session, simply highlight the **Exit Corrate** *option at the Main Menu, and press <CR>.*

INTERPRETATION OF THE RESULTS:

CCPP-

pH (eq) - The pH at equilibrium state.
CCPP - In mg/l as $CaCO_3$. A negative CCPP would indicate that the sample had not yet reached saturation point, whereas a positive value indicates that precipitation will occur.
Alk (eq) - The alkalinity at a state of equilibrium.

CORROSION RATE-

C-RATE (prog) - Corrosion Rate (calculated in microns per year) as calculated by the CORRATE program according to sample data.
C-RATE (TDS) - Corrosion Rate (in μ/y) as calculated according to TDS only.
C-RATE (COND) - Corrosion Rate (in μ/y) as calculated according to conductivity only.

Now, in the Corrosion Results output, there are two sets of results, namely

- Standard Results, meaning the corrosion rates for the original input data as it was entered.
- Equilibrium Results, meaning the corrosion rates for the data after it had reached a state of equilibrium.

Corrosion (μ/y) of

(i) < 50.8 - excellent water and pipe protection
(ii) 50.8 - 127 - good water and pipe protection
(iii) 127 - 254 - acceptable water and pipe protection
(iv) > 254 - corrosive water.

```
'****************************************************************************
'*                                                                          *
'*               A PROGRAM TO COMPUTE THE CCPP AND CORROSION                *
'*               RATES OF CERTAIN WATER SAMPLES, WRITTEN FOR                *
'*               THE EXPERIMENTAL WATER PURIFICATION PLANT                  *
'*               LABORATORY.                                                *
'*                                                                          *
'*               THE PROCEDURE TO CALCULATE THE CCPP VALUE                  *
'*               FIRST CALCULATES A "LEFT-HAND-SIDE" AND A                  *
'*               "RIGHT-HAND-SIDE", AND THEN COMPARES THESE                 *
'*               TWO VALUES. IF THEY ARE NOT WITHIN 10% OF  EACH            *
'*               OTHER, THEN A NEW PH IS TAKEN (ie. THE LOOP                *
'*               IS INCREMENTED BY 0.004).                                  *
'*                                                                          *
'*               CREATED TO RUN ON IBM PC/XT/AT COMPATABLES.                *
'*                                                                          *
'*               WINDOWS AND MENUS CREATED WITH TBWINDO.INC AND             *
'*               TBMENU.INC RESPECTIVELY, AND THE MAIN CODE                 *
'*               WITH BORLAND'S TURBO BASIC.                                *
'*                                                                          *
'*               BY D.A.BAXTER.                 29 APRIL 1992               *
'*                                                                          *
'****************************************************************************


$INCLUDE "TBWINDO.INC"
$INCLUDE "TBMENU.INC"


MW% = 10
ScrnArray = 3000


'----------------------------------------------------------------------------
'                            DISPLAY A WELCOME SCREEN
'
'----------------------------------------------------------------------------


CALL QFILL(1,1,25,80,32,FNATTR%(2,1))
CALL MAKEWINDOW(4,20,17,40,FNATTR%(0,7),2,1,1)
CALL PRTCWINDOW(2,"C O R R A T E")
CALL PRTCWINDOW(4,"Version 3.41")
CALL PRTCWINDOW(6,"Developed for the")
CALL PRTCWINDOW(7,"RAND WATER BOARD")
CALL PRTCWINDOW(8,"Laboratories")
CALL PRTCWINDOW(9,"Formulae Developed by")
CALL PRTCWINDOW(10,"Dr A.G.Brits.")
CALL PRTCWINDOW(11,"Programmed by")
CALL PRTCWINDOW(12,"D.A.Baxter. 13 Jan 1993")
CALL PRTCWINDOW(14,"Please Wait")

DELAY 5
```

```
CALL REMOVEWINDOW


'----------------------------------------------------------------------------
'                                DISPLAY A POINT-AND-SHOOT TYPE MENU
'
'----------------------------------------------------------------------------

START:


pHeq = 0


BEEP

ITEM$(1) = "Calculate CCPP"
ITEM$(2) = "Calculate Corrosion"
ITEM$(3) = "Exit Corrate"

ITEMCOUNT% = 3
MTITLE$ = " [ MAIN MENU ] "
MROW% = 8
MCOL% = 20
MWIDTH% = 40
MATTR% = FNATTR%(15,1)
MHIATTR% = FNATTR%(0,7)
MRBDRSEL% = 2
MSHADOW% = 1
MZOOM% = 0
STARTPOS% = 1

RESTART1:



CALL QFILL(1,1,25,80,32,FNATTR%(0,7))

CALL MAKEMENU

SELECT CASE CURNTPOS%
       CASE 1
            GOSUB PRECIPITATEPOTENCIAL
            GOTO RESTART1
       CASE 2
            GOSUB CORROSIONRATE
            GOTO RESTART1
       CASE 3
            COLOR 7,0
            CLS
            END
END SELECT



'----------------------------------------------------------------------------
'                                LOOP FOR CCPP
```

```
'
'------------------------------------------------------------------------------


PRECIPITATEPOTENCIAL:



'-------------------- DISPLAY A HEADING INPUT SCREEN -------------------------


COLOR 1,7
    CALL QFILL(1,1,25,80,32,FNATTR%(2,1))
    CALL MAKEWINDOW(9,20,5,40,FNATTR%(0,7),2,1,1)
         CALL TITLEWINDOW(2,"[ SAMPLE INPUT ]")
         CALL PRTCWINDOW(2,"PLEASE ENTER THE SAMPLE NAME")
         CALL PRTCWINDOW(3,"[                                 ]")
              LOCATE 12,25
              INPUT SAMPLENAME$

SAMPLENAMELENGTH% = LEN(SAMPLENAME$)
MIDDLE% = INT((70-SAMPLENAMELENGTH%)/2)



'------------------ DISPLAY AN INPUT SCREEN FOR CCPP DATA --------------------



COLOR 6,7
    CALL QFILL(1,1,25,80,32,FNATTR%(2,1))
    CALL MAKEWINDOW(2,20,20,40,FNATTR%(0,7),2,1,1)
         CALL TITLEWINDOW(2,"[ INPUT FOR CCPP ]")
         CALL PRTCWINDOW(2,"ENTER CALCIUM IN mg/l")
         CALL PRTCWINDOW(3,"[            ]")
         CALL PRTCWINDOW(4,"ENTER ALKALINITY IN mg/l")
         CALL PRTCWINDOW(5,"[            ]")
         CALL PRTCWINDOW(6,"ENTER THE INITIAL pH")
         CALL PRTCWINDOW(7,"[            ]")
         CALL PRTCWINDOW(8,"ENTER THE TEMP. (deg C)")
         CALL PRTCWINDOW(9,"[            ]")
         CALL PRTCWINDOW(10,"ENTER THE SAMPLE'S TDS")
         CALL PRTCWINDOW(11,"[            ]")
         CALL PRTCWINDOW(12,"ENTER CONDUCTIVITY (mS/m)")
         CALL PRTCWINDOW(13,"[            ]")
              LOCATE 5,35
              INPUT ca
              LOCATE 7,35
              INPUT alkalinity
              LOCATE 9,35
              INPUT ph
              LOCATE 11,35
              INPUT temperature
              LOCATE 13,35
              INPUT tds
              LOCATE 15,35
              INPUT CONDUCTIVITY
         CALL PRTCWINDOW(15,"VALUES CORRECT ? (y=yes, n=no)")
         CALL PRTCWINDOW(16,"[          ]")
```

```
              LOCATE 18,35
              INPUT ANS$
         CALL PRTCWINDOW(18,"PLEASE WAIT")

'------------------------ TEST FOR BAD VALUES ----------------------------------


IF (ca < 0) OR (ca > 1000) THEN GOTO BADVAL
IF (alkalinity < 0) OR (alkalinity > 1000) THEN GOTO BADVAL
IF (temperature < 0) OR (temperature > 100) THEN GOTO BADVAL
IF (tds < 0) OR (tds > 1000) THEN GOTO BADVAL
IF (ph < 0) OR (ph > 14) THEN GOTO BADVAL



IF (ANS$=CHR$(78)) OR (ANS$=CHR$(110)) THEN GOTO PRECIPITATEPOTENCIAL
IF NOT((ANS$=CHR$(89)) OR (ANS$=CHR$(121))) THEN GOTO PRECIPITATEPOTENCIAL




'---------------------- LOOP FOR CCPP PROGRAM ----------------------------------



Alk = (alkalinity*0.00002)
CALCIUM = Ca * 25 * 10^(-6)
TEMP = TEMPERATURE + 273
I = TDS / 40000
A = 1820000 * ((78.3 * TEMP) ^ -1.5)
pfm = A * (SQR(I)/(1+SQR(I))) - (A * (0.3*I))
Hi = 10 ^ (pfm - pH)
pk1 = (17052/TEMP) + (215.21*log10(TEMP)) - (0.12675*TEMP) - 545.56
pk2 = 107.8871 + 0.03252849*TEMP - 5151.79/TEMP - 38.92561*log10(TEMP)_
      + 563713.9/(TEMP^2)
pkw = 4471/TEMP + 0.01706*TEMP - 6.0875
pksc = 171.9065 + 0.077993*TEMP - 2839.319/TEMP - 71.595*log10(TEMP)
k1 = 10^((2*pfm)-pk1)
k2 = 10^((4*pfm)-pk2)
kw = 10^((2*pfm)-pkw)
ks = 10^((8*pfm)-pksc)
p = ((2*Hi) + k1)/k1
t = ((2*k2) + Hi)/Hi
s = (Hi-(kw/Hi))
ACIDITY = (((Alk + s)/ t) * p) + s
pHeq = 6.996
DIFF = 20
DIFFERENCE = 20
  WHILE DIFFERENCE >= 20
    pHeq = pHeq + 0.004
    Heq = 10^(pfm - pHeq)
    peq = ((2*Heq) + k1)/k1
    req = ((2*k2) + Heq)/k2
    teq = ((2*k2) + Heq)/Heq
    seq = (Heq - (kw/Heq))
    LHS = 2*CALCIUM - Alk
```

```
    IF LHS = 0 THEN LHS = 0.001
    RHS = ((2*ks*req*peq)/(teq*(ACIDITY - seq))) - ((teq*(ACIDITY - seq))/peq)_
        + seq
    IF LHS > RHS THEN DIFFERENCE = ((LHS-RHS)/LHS)*100
    IF RHS > LHS THEN DIFFERENCE = ((RHS-LHS)/RHS)*100
    IF DIFFERENCE < 0 THEN DIFFERENCE = DIFFERENCE * (-1)
    if pHeq >=14 then GOTO BADVAL
  WEND


RETURNLOOP:

  IF DIFFERENCE <= DIFF THEN GOSUB STOREVALUES
  IF DIFFERENCE <= DIFF THEN DIFF = DIFFERENCE
  IF DIFFERENCE <= DIFF THEN GOTO INNERLOOP
  GOSUB RETRIEVEVALUES



CALCULATECCPP:

Alkeq = ((teq/peq) * (ACIDITY - seq)) - seq
CCPP = 50000 * (Alk - Alkeq)


CALL REMOVEWINDOW



'------------------------ OUTPUT THESE RESULTS -------------------------------


COLOR 1,7
    CALL QFILL(1,1,25,80,32,FNATTR%(2,1))
    CALL MAKEWINDOW(6,20,14,40,FNATTR%(0,7),2,1,1)
         CALL TITLEWINDOW(2,"[ CCPP RESULTS ]")
            CALL PRTCWINDOW(2,"Alkalinity = ")
                 LOCATE 8,45
                 PRINT USING "#####.###";(Alkeq/0.00002)
            CALL PRTCWINDOW(4,"pH (eq)     = ")
                 LOCATE 10,45
                 PRINT USING "#####.###";pheq
            CALL PRTCWINDOW(6,"CCPP        = ")
                 LOCATE 12,45
                 PRINT USING "#####.###";CCPP
            CALL PRTCWINDOW(9,"PRINT THESE RESULTS ? (y=yes, n=no)")
            CALL PRTCWINDOW(10,"[           ]")
                 LOCATE 16,35
                 INPUT PRINTEROUT$

IF (PRINTEROUT$=CHR$(78)) OR (PRINTEROUT$=CHR$(110)) THEN RETURN
IF NOT((PRINTEROUT$=CHR$(89)) OR (PRINTEROUT$=CHR$(121))) THEN RETURN


'-------------------------- OUTPUT DATA TO PRINTER --------------------------
```

```
CALL PRTCWINDOW(12,"PRINTING - PLEASE WAIT ...")


LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT TAB(MIDDLE%);SAMPLENAME$
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT "                              CCPP RESULTS"
LPRINT "======================================================================'
LPRINT
LPRINT
LPRINT TAB(5);DATE$,TAB(57);TIME$
LPRINT
LPRINT
LPRINT
LPRINT "                             INPUT DATA -"
LPRINT "                             -----------
LPRINT
LPRINT
LPRINT "          Calcium (mg/l)    = ",USING "####.###";ca
LPRINT "          Alkalinity        = ",USING "####.###";alkalinity
LPRINT "          Initial pH        = ",USING "####.###";pH
LPRINT "          TDS               = ",USING "####.###";tds
LPRINT "          Temperature (C)   = ",USING "####.###";temperature
LPRINT "          Conductivity      = ",USING "####.###";CONDUCTIVITY
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT "                             OUTPUT DATA -"
LPRINT "                             ------------"
LPRINT
LPRINT
LPRINT "          Alk (eq)          = ",USING "####.###";Alkeq/0.00002
LPRINT "          pH (eq)           = ",USING "####.###";pHeq
LPRINT "          CCPP              = ",USING "####.###";CCPP
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT "---------------------------------------------------------------------
LPRINT
LPRINT
LPRINT
LPRINT
```

```
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT


CALL REMOVEWINDOW

RETURN


CORROSIONRATE:




'--------------------------------------------------------------------------------
'                              LOOP FOR CORROSION RATE
'
'--------------------------------------------------------------------------------


ITEM$(1) = "Calculate Corrosion Rate"
ITEM$(2) = "New CCPP data values"
ITEM$(3) = "Quit to Main Menu"
ITEMCOUNT% = 3
MTITLE$ = " [ CORROSION MENU ] "
MROW% = 8
MCOL% = 20
MWIDTH% = 40
MATTR% = FNATTR%(15,1)
MHIATTR% = FNATTR%(0,7)
MRBDRSEL% = 2
MSHADOW% = 1
MZOOM% = 0
STARTPOS% = 1


CRATE:
CALL QFILL(1,1,25,80,32,FNATTR%(0,7))

CALL MAKEMENU

SELECT CASE CURNTPOS%
     CASE 1
          GOSUB CORROSIONRUN
          GOTO CRATE
     CASE 2
          GOSUB NEWDATA
          GOTO CRATE
     CASE ELSE
          GOTO START
```

```
RETURN
END SELECT


'------------------------------ NEWDATA ------------------------------------


NEWDATA:


'--------------------------- SAMPLE NAME INPUT -----------------------------

COLOR 1,7
    CALL QFILL(1,1,25,80,32,FNATTR%(2,1))
    CALL MAKEWINDOW(9,20,5,40,FNATTR%(0,7),2,1,1)
         CALL TITLEWINDOW(2,"[ SAMPLE INPUT ]")
         CALL PRTCWINDOW(2,"PLEASE ENTER THE SAMPLE NAME")
         CALL PRTCWINDOW(3,"[                                  ]")
              LOCATE 12,25
              INPUT SAMPLENAME$


SAMPLENAMELENGTH% = LEN(SAMPLENAME$)
MIDDLE% = INT((70-SAMPLENAMELENGTH%)/2)


CALL REMOVEWINDOW



COLOR 6,7
    CALL QFILL(1,1,25,80,32,FNATTR%(2,1))
    CALL MAKEWINDOW(4,20,15,40,FNATTR%(0,7),2,1,1)
    CALL TITLEWINDOW(2,"[ NEW CORROSION-RATE INPUT DATA ]")
         CALL PRTCWINDOW(2,"ENTER NEW CCPP VALUE")
         CALL PRTCWINDOW(3,"[             ]")
         CALL PRTCWINDOW(4,"ENTER NEW ALKALINITY")
         CALL PRTCWINDOW(5,"[             ]")
         CALL PRTCWINDOW(6,"ENTER THE NEW pH")
         CALL PRTCWINDOW(7,"[             ]")
         CALL PRTCWINDOW(8,"ENTER THE CONDUCTIVITY")
         CALL PRTCWINDOW(9,"[             ]")
         CALL PRTCWINDOW(10,"ENTER TEMPERATURE (DEG C)")
         CALL PRTCWINDOW(11,"[            ]")
         CALL PRTCWINDOW(12,"ENTER SAMPLE'S TDS")
         CALL PRTCWINDOW(13,"[            ]")
              LOCATE 7,35
              INPUT CCPP
              LOCATE 9,35
              INPUT alkalinity
              LOCATE 11,35
              INPUT ph
              LOCATE 13,35
              INPUT CONDUCTIVITY
              LOCATE 15,35
              INPUT TEMPERATURE
              LOCATE 17,35
              INPUT tds
```

```
CALL REMOVEWINDOW

RETURN


'------------------------- CORROSION RATE PROGRAM ---------------------------


CORROSIONRUN:


COLOR 6,7
    CALL QFILL(1,1,25,80,32,FNATTR%(2,1))
    CALL MAKEWINDOW(6,20,13,40,FNATTR%(0,7),2,1,1)
         CALL TITLEWINDOW(2,"[ DATA INPUT FOR CORROSION RATES  ]")
         CALL PRTCWINDOW(2,"ENTER THE Cl VALUE")
         CALL PRTCWINDOW(3,"[               ]")
         CALL PRTCWINDOW(4,"ENTER THE SO4 VALUE")
         CALL PRTCWINDOW(5,"[               ]")
         CALL PRTCWINDOW(6,"ENTER THE N VALUE")
         CALL PRTCWINDOW(7,"[               ]")
         CALL PRTCWINDOW(8,"ENTER THE Cl2 VALUE")
         CALL PRTCWINDOW(9,"[               ]")
         CALL PRTCWINDOW(10,"ENTER THE %O2 VALUE")
         CALL PRTCWINDOW(11,"[               ]")
              LOCATE 9,35
              INPUT cl
              LOCATE 11,35
              INPUT so4
              LOCATE 13,35
              INPUT n
              LOCATE 15,35
              INPUT cl2
              LOCATE 17,35
              INPUT O2


'--------------------------- DATA MANIPULATION ----------------------------


FACTOR1 =  ((8.87*10^(-4)) * O2) + 0.915
FACTOR2 =  ((2.25*10^(-2)) * TEMPERATURE) + 0.503


no3 = n * 4.43


'-------------------- CORROSION RATES ON THE ORIGINAL DATA -----------------
```

```
CROLD = (((0.161*cl) + (0.158*so4) + (0.12*cl2) + (0.379*no3) +_
        (0.123*ALKALINITY) + (0.389*ph) - 4.64) * FACTOR1 * FACTOR2) * 25.4
OLDTDS = tds
CRTDSOLD = (((0.0748 * tds) - 0.151) * FACTOR1 * FACTOR2) * 25.4
IONSTROLD = tds * (2.5*10^(-5))
CONDOLD = CONDUCTIVITY
CRCONOLD = (((0.5059*CONDOLD) - 0.1866) * FACTOR1 * FACTOR2) * 25.4


'---------------- CORROSION RATES ON THE EQUILIBRIUM DATA -------------------


pHEQUAT = ph

IF (pHeq > 0) AND (pHeq < 13.9) THEN pHEQQUAT = pHeq


CR = (((0.161*cl)+(0.158*so4)+(0.12*cl2)+(0.379*no3)+_
     (0.123*(ALKALINITY-CCPP))+(0.389*pHEQUAT)-4.64) * FACTOR1 * FACTOR2) * 25.

tds = tds - CCPP

CRTDS = (((0.0748*tds) - 0.151) * FACTOR1 * FACTOR2) * 25.4

IONSTR = tds * (2.5 * 10 ^ (-5))
CONDUCTIVITY = IONSTR / (1.68 * 10 ^ (-4))

CRCON = (((0.5059*CONDUCTIVITY) - 0.1866) * FACTOR1 * FACTOR2) * 25.4


'------------------------ END OF CORROSION CODING ----------------------------




CALL REMOVEWINDOW


'---------------------------- OUTPUT THESE RESULTS ----------------------------


COLOR 1,7
    CALL QFILL(1,1,25,80,32,FNATTR%(2,1))
    CALL MAKEWINDOW(6,20,12,40,FNATTR%(0,7),2,1,1)
         CALL TITLEWINDOW(2,"[ CORROSION-RATE RESULTS ]")
            CALL PRTCWINDOW(3,"C-RATE (prog)  :  ")
                 LOCATE 9,45
                 PRINT USING "####.###";CR
            CALL PRTCWINDOW(4,"C-RATE (TDS)   :  ")
                 LOCATE 10,45
```

```
                 PRINT USING "####.###";CRTDS
            CALL PRTCWINDOW(5,"C-RATE (COND)   :   ")
                 LOCATE 11,45
                 PRINT USING "####.###";CRCON
            CALL PRTCWINDOW(7,"PRINT THESE RESULTS ? (y=yes, n=no)")
            CALL PRTCWINDOW(8,"[          ]")
                 LOCATE 14,35
                 INPUT PRINTAGAIN$

IF (PRINTAGAIN$=CHR$(78)) OR (PRINTAGAIN$=CHR$(110)) THEN RETURN
IF NOT((PRINTAGAIN$=CHR$(89)) OR (PRINTAGAIN$=CHR$(121))) THEN RETURN


'---------------------------- OUTPUT DATA TO PRINTER ------------------------


COLOR 6,7
CALL PRTCWINDOW(10,"PRINTING - PLEASE WAIT ...")


'------------------------- CODE FOR DETERMINIMG CORROSIVITY ------------------


IF (CROLD < 50.8) THEN AA$ = "EXCELLENT"
IF (CROLD >= 50.8) AND (CROLD <= 127) THEN AA$ = "GOOD"
IF (CROLD > 127) AND (CROLD <= 254) THEN AA$ = "ACCEPTABLE"
IF (CROLD > 254) THEN AA$ = "CORROSIVE"


IF (CRTDSOLD < 50.8) THEN AB$ = "EXCELLENT"
IF (CRTDSOLD >= 50.8) AND (CRTDSOLD <= 127) THEN AB$ = "GOOD"
IF (CRTDSOLD > 127) AND (CRTDSOLD <= 254) THEN AB$ = "ACCEPTABLE"
IF (CRTDSOLD > 254) THEN AB$ = "CORROSIVE"


IF (CRCONOLD < 50.8) THEN AC$ = "EXCELLENT"
IF (CRCONOLD >= 50.8) AND (CRCONOLD <= 127) THEN AC$ = "GOOD"
IF (CRCONOLD > 127) AND (CRCONOLD <= 254) THEN AC$ = "ACCEPTABLE"
IF (CRCONOLD > 254) THEN AC$ = "CORROSIVE"


IF (CR < 50.8) THEN BA$ = "EXCELLENT"
IF (CR >= 50.8) AND (CR <= 127) THEN BA$ = "GOOD"
IF (CR > 127) AND (CR <= 254) THEN BA$ = "ACCEPTABLE"
IF (CR > 254) THEN BA$ = "CORROSIVE"



IF (CRTDS < 50.8) THEN BB$ = "EXCELLENT"
IF (CRTDS >= 50.8) AND (CRTDS <= 127) THEN BB$ = "GOOD"
IF (CRTDS > 127) AND (CRTDS <= 254) THEN BB$ = "ACCEPTABLE"
IF (CRTDS > 254) THEN BB$ = "CORROSIVE"


IF (CRCON < 50.8) THEN BC$ = "EXCELLENT"
IF (CRCON >= 50.8) AND (CRCON <= 127) THEN BC$ = "GOOD"
IF (CRCON > 127) AND (CRCON <= 254) THEN BC$ = "ACCEPTABLE"
IF (CRCON > 254) THEN BC$ = "CORROSIVE"
```

```
'--------------------------- BEGIN PRINTOUT ----------------------------------


LPRINT
LPRINT
LPRINT
LPRINT TAB(MIDDLE%);SAMPLENAME$
LPRINT
LPRINT
LPRINT "                          CORROSION RESULTS"
LPRINT "======================================================================'
LPRINT
LPRINT
LPRINT
LPRINT TAB(5);DATE$,TAB(55),TIME$
LPRINT
LPRINT
LPRINT
LPRINT "                              INPUT DATA-"
LPRINT "                              ----------"
LPRINT
LPRINT
LPRINT "          pH                =",USING "####.###";ph
LPRINT "          Alkalinity        =",USING "####.###";alkalinity
LPRINT "          pH (eq)           =",USING "####.###";pHeq
LPRINT "          Alk (eq)          =",USING "####.###";Alkeq/0.00002
LPRINT "          CCPP              =",USING "####.###";CCPP
LPRINT "          Cl                =",USING "####.###";cl
LPRINT "          SO4               =",USING "####.###";so4
LPRINT "          NO3               =",USING "####.###";no3
LPRINT "          Cl2               =",USING "####.###";cl2
LPRINT "          % Oxygen          =",USING "####.###";O2
LPRINT "          Orig. Conductiv.  =",USING "####.###";CONDOLD
LPRINT "          Orig. TDS         =",USING "####.###";OLDTDS
LPRINT "          Conductivity (eq) =",USING "####.###";CONDUCTIVITY
LPRINT "          TDS (eq)          =",USING "####.###";tds
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT "                              OUTPUT DATA-"
LPRINT "                              -----------"
LPRINT
LPRINT "                  Results expressed in microns per year"
LPRINT
LPRINT "      BEFORE EQUILIBRIUM :"
LPRINT
LPRINT "      C-RATE - prog         =",AA$,USING "####.###";CROLD
LPRINT "      C-RATE - TDS          =",AB$,USING "####.###";CRTDSOLD
LPRINT "      C-RATE - conductivity =",AC$,USING "####.###";CRCONOLD
LPRINT
LPRINT
LPRINT "      AT EQUILIBRIUM :"
LPRINT
LPRINT "      C-RATE - prog         =",BA$,USING "####.###";CR
LPRINT "      C-RATE - TDS          =",BB$,USING "####.###";CRTDS
```

```
LPRINT "       C-RATE - conductivity =",BB$,USING "####.###";CRCON
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT "----------------------------------------------------------------------"
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT
LPRINT


CALL REMOVEWINDOW

RETURN



BADVAL:

'----------------------------------------------------------------------
'                              LOOP FOR BADVALUE
'
'----------------------------------------------------------------------


SOUND 100,9
CLS

COLOR 0,7
    CALL QFILL(1,1,25,80,32,FNATTR%(2,1))
    CALL MAKEWINDOW(8,20,7,40,FNATTR%(0,7),2,1,1)
         CALL PRTCWINDOW(2,"BAD INPUT DATA - PLEASE")
         CALL PRTCWINDOW(3,"ENTER NEW DATA AT PROMPT")
         CALL PRTCWINDOW(5,"PLEASE WAIT ...")

DELAY 5

CALL REMOVEWINDOW

GOTO RESTART1


'----------------------------------------------------------------------
'                              LOOP FOR RESTOREVALUES
'----------------------------------------------------------------------

STOREVALUES:

DIFFER = DIFFERENCE
PHEQUIL = pHeq
H = Heq
p = peq
r = req
```

```
t = teq
s = seq

RETURN



'---------------------------------------------------------------------------------
'                              LOOP FOR RETRIEVEVALUES
'---------------------------------------------------------------------------------

RETRIEVEVALUES:

DIFFERENCE = DIFFER
pHeq = PHEQUIL
Heq = H
peq = p
req = r
teq = t
seq = s

RETURN



'---------------------------------------------------------------------------------
'                                INNER LOOP
'---------------------------------------------------------------------------------


INNERLOOP:

    pHeq = pHeq + 0.001
    Heq = 10^(pfm - pHeq)
    peq = ((2*Heq) + k1)/k1
    req = ((2*k2) + Heq)/k2
    teq = ((2*k2) + Heq)/Heq
    seq = (Heq - (kw/Heq))
    LHS = 2*CALCIUM - Alk
    IF LHS = 0 THEN LHS = 0.001
    RHS = ((2*ks*req*peq)/(teq*(ACIDITY - seq))) - ((teq*(ACIDITY - seq))/peq)_
         + seq
    IF LHS > RHS THEN DIFFERENCE = ((LHS-RHS)/LHS)*100
    IF RHS > LHS THEN DIFFERENCE = ((RHS-LHS)/RHS)*100
    IF DIFFERENCE < 0 THEN DIFFERENCE = DIFFERENCE * (-1)
    if pHeq >=14 then GOTO BADVAL

GOTO RETURNLOOP


'---------------------------- END OF PROGRAM CORRATE ------------------------

END
```

APPENDIX H

LABORATORY ANALYTICAL METHOD AND WORKSHEET

APPENDIX H

LABORATORY ANALYTICAL METHOD AND WORKSHEET

Analytical method for determining

- Calcium Carbonate Precipitation Potential (CCPP)
- Alkalinity, Calcium and pH for initial and equilibrium conditions
- Langelier Saturation Index
- Worksheet for calculating and reporting corrosiveness of water towards mild steel
- Interpretation of corrosion rates based on chemical composition

RAND WATER

Empirical methods to determining the **Calcium Carbonate Precipitation Potential (CCPP), saturation alkalinity (Alksat), saturation calcium (Casat) and saturation pH (pHsat)** of potable water.

SCOPE

This method is an adaption of DIN 38 404-C10-1 and is intended to measure the pH, alkalinity and calcium of water after it has been saturated with calcium carbonate under controlled conditions. From the difference between the original alkalinity and/or calcium content, and the alkalinity and/or calcium after saturation, the Calcium Carbonate Precipitation Potential (CCPP) can be determined. The difference between the original pH and saturation pH can be applied to determine whether the water is under or over saturated.

EQUIPMENT AND REAGENTS

In addition to the standard equipment usually available in a chemical laboratory, the following will be required:

Glassware

Shall be of borosilicate glass and include:
- Two conical flasks of 0,5 l capacity with stoppers.
- Two 250 ml measuring cylinders.
- Two 250 ml beakers.

Apparatus
- Two magnetic stirrers with suitably encapsulated stirrer bars.
- A pH meter for measurements in accordance with the latest issue of SABS Method 11.
- A mechanical shaker for sample preparation. (This is optional, but is of great assistance if a large number of samples have to be analysed).

Reagents
- Calcium carbonate, precipitated, chemically pure or reagent grade.
- Freshly prepared distilled water.

PROCEDURES

Preparing the sample

As dissolved gases may influence the end results it is essential that loss of these to the atmosphere be **minimised**. It is therefore recommended that the sample be **well-chilled** in its original sealed container, **shaken vigorously** to reincorporate any gases that may have evaporated into the head space, and transferred by **siphon** (in preference to being poured) into the reaction vessel.

Calibrating the reaction flask

Use the measuring cylinder to transfer 250 ml of distilled water **into two conical flasks** and carefully mark the water levels by means of a suitable pen. Discard the water and then allow the two **flasks** to drain thoroughly.

Standard procedure

Siphon off approximately **250 ml of each sample** into two conical reaction flasks, using the previously established calibration marks to estimate the level to which the flasks should be filled. Add 2 ± 0,5 g of calcium carbonate in one flask, insert the stirrer bar and stopper into each flask. Place flasks onto two separate magnetic stirrer platforms and adjust the speed to give a stirring action just sufficient to keep the calcium carbonate in suspension. The flask without calcium carbonate acts as a reference. At the end of **20 minutes**, during which time the temperature of the prechilled sample may be allowed to slowly rise to room temperature, make a further addition of the same quantity of calcium carbonate to the flask containing the first batch of calcium carbonate and stir for a further period of 20 minutes. Allow the excess calcium carbonate to settle, adjust the temperature to 20 ± 2°C if necessary, decant the clear solution in the flask containing the calcium carbonate into a clean, dry beaker. Determine pH, Alk and Ca for the sample in flask without calcium carbonate and the pH, Alk and Ca of the decanted clear solution from the flask containing calcium carbonate. If it is only the aim to determine if the water is under or over saturated with calcium carbonate the pH of both solutions as prepared above must be measured. If the aim is to obtain the CCPP of the original water the alkalinity and/or calcium content of both prepared solutions (before and after calcium carbonate addition) must be determined.

Shortened procedure

If it is known that the sample is free of Fe ions, or if the Fe content is less than 5 mg/l, the standard procedure may be shortened by adding the full quantity of calcium carbonate initially and stirring for only one 15 minute period.

REPORTING THE RESULTS

1. Report the pH before calcium carbonate saturation as pH_{init} and after saturation as pH_{sat}.

2. Report the alkalinity before calcium carbonate saturation as Alk_{init} and after saturation as Alk_{sat}.

3. Report the calcium before calcium carbonate saturation as Ca_{init} and after saturation as Ca_{sat}.

APPLICATION

1. The calcium carbonate precipitation potential can be obtained by:

$CCPP = Alk_{init} - Alk_{sat}$ . . . . (1)

and/or

$CCPP = Ca_{init} - Ca_{sat}$ . . . . (2)

with Alk_{init}, Alk_{sat}, Ca_{init} and Ca_{sat} express as mg/l $CaCO_3$.

If the result of calculations (1) and (2) are negative, precipitated calcium carbonate (scale) will dissolve and if the result is positive, calcium carbonate will precipitate (scale formation).

2(a) The saturation state of the water can be obtained by:

Saturation state $= pH_{init} - pH_{sat}$ . . . . (3)

If the result of calculation (3) is negative the water is under saturated and if it is positive the water is over saturated with calcium carbonate.

(b) The Langelier index can be calculated by making use of the equation

$LI = pH_{init} - pH_{sat}$.

WORKSHEET AND REPORT TO BE USED WITH LABORATORY METHOD

SAMPLE NO.................... DATE.......................

ORIGIN OF SAMPLE.......................................

Corrosiveness OF POTABLE WATER ON MILD STEEL.

Only one or any combination of (a), (b), and (c) may be used.

a) CORROSION EQUATION

Analysis		Equations	Values
Chloride (mg/ℓ)	A_1 =	$A_1 \times 4{,}09$	B_1 =
Sulphate (mg/ℓ)	A_2 =	$A_2 \times 4{,}03$	B_2 =
Chlorine (mg/ℓ as Cl_2)	A_3 =	$A_3 \times 2{,}79$	B_3 =
Nitrate (mg/ℓ as N)	A_4 =	$A_4 \times 9{,}78$	B_4 =
Talk as mg/ℓ $CaCO_3$	A_5 =	$A_5 \times 3{,}12$	B_5 =
*CCPP as mg/ℓ $CaCO_3$	A_6 =	$A_6 \times 3{,}12$	B_6 =
pH	A_7 =	$A_7 \times 9{,}98 - 119$	B_7 =
F1 (% dissolved 0_2)	A_8 =	$A_8 \times 8{,}81 \times 10^{4} + 0{,}919$	B_8 =
F2 (temperature in °C)	A_9 =	$A_9 \times 2{,}25 \times 10^{2} + 0{,}509$	B_9 =

* CCPP as determined by laboratory method - "Marble test"

Corrosiveness in micron per year;

$[B1 + B2 + B3 + B4 + (B5 - B6/B8) + B7] \times B8 \times B9 =$ .... µm/y

b) TOTAL DISSOLVED SOLIDS IN mg/l (TDS)

Corrosiveness in micron per year;

$1{,}9 \times TDS - 3{,}84 =$ .... µm/y

c) CONDUCTIVITY IN mS/m

Corrosiveness in micron per year;

12,85 mS/m - 4,74 = ... µm/y

INTERPRETATION OF THE CALCULATED CORROSION RATES PRODUCED

The calculated result can now be compared with the Middelsex Water Company's index;

CORROSION RATE	WATER QUALITY
• <51 micron per year	indicates both excellent water quality and pipeline protection
• 51-127 micron per year	indicates good water quality and protection
• 127-254 micron per year	indicates water of acceptable quality
• >250 micron per year	indicates corrosive water

If this index indicates a water that is corrosive but with a positive CCPP value this water will still provide pipe protection.